

Comparative STM analysis of C60 and C70 fullerene adsorption sites on pristine and Al-modified Si(111)7×7 surfaces

Vsevolod V. Mararov, Dimitry V. Gruznev, Leonid V. Bondarenko, Alexandra Y. Tupchaya, Andrey V. Zotov, and Alexander A. Saranin

Citation: *Journal of Vacuum Science & Technology A* **34**, 061402 (2016); doi: 10.1116/1.4963067

View online: <http://dx.doi.org/10.1116/1.4963067>

View Table of Contents: <http://scitation.aip.org/content/avs/journal/jvsta/34/6?ver=pdfcov>

Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Articles you may be interested in

[Incommensurate superstructure in heavily doped fullerene layer on Bi/Si\(111\) surface](#)

J. Chem. Phys. **143**, 074707 (2015); 10.1063/1.4928866

[Preserving the 7×7 surface reconstruction of clean Si\(111\) by graphene adsorption](#)

Appl. Phys. Lett. **107**, 071603 (2015); 10.1063/1.4928930

[Initial and secondary oxidation products on the Si\(111\)-\(7×7\) surface identified by atomic force microscopy and first principles calculations](#)


Appl. Phys. Lett. **104**, 133107 (2014); 10.1063/1.4870629





[Adsorption and dissociation of oxygen molecules on Si\(111\)-\(7×7\) surface](#)

J. Chem. Phys. **139**, 194709 (2013); 10.1063/1.4832340

[Antimony adsorption on the Si\(111\) surface with the 7×7 and √3×√3-Ga structures studied by scanning tunneling microscopy](#)

J. Vac. Sci. Technol. A **15**, 1603 (1997); 10.1116/1.580639


Instruments for Advanced Science

<p>Contact Hiden Analytical for further details: W www.HidenAnalytical.com E info@hiden.co.uk</p> <p>CLICK TO VIEW our product catalogue</p>	 <p>Gas Analysis</p> <ul style="list-style-type: none"> › dynamic measurement of reaction gas streams › catalysis and thermal analysis › molecular beam studies › dissolved species probes › fermentation, environmental and ecological studies 	 <p>Surface Science</p> <ul style="list-style-type: none"> › UHV TPD › SIMS › end point detection in ion beam etch › elemental imaging - surface mapping 	 <p>Plasma Diagnostics</p> <ul style="list-style-type: none"> › plasma source characterization › etch and deposition process reaction › kinetic studies › analysis of neutral and radical species 	 <p>Vacuum Analysis</p> <ul style="list-style-type: none"> › partial pressure measurement and control of process gases › reactive sputter process control › vacuum diagnostics › vacuum coating process monitoring
--	--	--	--	--

Comparative STM analysis of C₆₀ and C₇₀ fullerene adsorption sites on pristine and Al-modified Si(111)7 × 7 surfaces

Vsevolod V. Mararov, Dmitry V. Gruznev, Leonid V. Bondarenko, and Alexandra Y. Tupchaya

Institute of Automation and Control Processes FEB RAS, 5 Radio Street, 690041 Vladivostok, Russia and School of Natural Sciences, Far Eastern Federal University, 690950 Vladivostok, Russia

Andrey V. Zotov^{a)}

Institute of Automation and Control Processes FEB RAS, 5 Radio Street, 690041 Vladivostok, Russia; School of Natural Sciences, Far Eastern Federal University, 690950 Vladivostok, Russia; and Department of Electronics, Vladivostok State University of Economics and Service, 690600 Vladivostok, Russia

Alexander A. Saranin

Institute of Automation and Control Processes FEB RAS, 5 Radio Street, 690041 Vladivostok, Russia and School of Natural Sciences, Far Eastern Federal University, 690950 Vladivostok, Russia

(Received 7 June 2016; accepted 6 September 2016; published 20 September 2016)

Using scanning tunneling microscopy observations, preferable adsorption sites of C₆₀ and C₇₀ fullerenes on pristine Si(111)7 × 7 and Al-modified Si(111)α-7 × 7-Al surfaces at 300 and 450 K were determined. The C₆₀ and C₇₀ molecules display similar, albeit not identical, adsorption behavior while the most essential variance is related with the hosting surfaces, pristine 7 × 7 or α-7 × 7-Al. Both C₆₀ and C₇₀ prefer to occupy positions above the Si rest atoms upon adsorption onto Si(111)7 × 7 at 300 K and change their preferable sites for those located at the Si edge adatom at 450 K, that is plausibly accompanied by releasing the Si adatom. Upon C₆₀ and C₇₀ adsorption onto Si(111)α-7 × 7-Al surface at 300 K, the fullerenes prefer to occupy the asymmetric sites at the dimer rows. At 450 K, the C₇₀ fullerenes preserve this location, while about half of the C₆₀ fullerenes change it for that at the corner Si adatom position. The present experimental data set serves as a useful basis for theoretical analysis. © 2016 American Vacuum Society.

[<http://dx.doi.org/10.1116/1.4963067>]

I. INTRODUCTION

Since seminal discovery of the C₆₀ buckminsterfullerene in 1985,¹ the fullerenes, a family of carbon molecules having a cage structure, have attracted a wide attention due to their unique structural and electronic properties. Growth of fullerene films on various substrates is the actively developed research area of numerous investigations. Elucidating the adsorption geometry and interactions of a single fullerene molecule with a surface is very important for understanding the mechanisms of fullerene self-assembly. Scanning tunneling microscopy (STM) is believed to be the most feasible tool to fix directly the adsorption sites occupied by the fullerenes on a given surface. In the present work, adsorption of individual fullerenes onto the surface has been studied using STM with three growth parameters being varied.

First, two types of fullerenes have been used, C₆₀ and C₇₀. The C₆₀ molecule is the most abundant form of fullerenes, which consists of 20 hexagonal and 12 pentagonal carbon rings and has a shape of sphere. The C₇₀ is the second most stable and abundant fullerene. It incorporates five additional hexagonal rings in its equatorial plane, hence having a slightly elongated shape [Fig. 1(a)]. Compared to C₆₀ molecules, C₇₀ on surfaces have been far less studied.

Second, two types of parent surfaces have been used, pristine and Al-modified Si(111)7 × 7. The pristine Si(111)7 × 7

surface has a well-known dimer-adatom-stacking fault structure² consisting of two triangular half unit cells (HUCs), faulted and unfaulted, and a corner hole. Each half unit cell contains nine dangling-bond atoms (which are of the most essence for adsorption) including six adatoms and three rest atoms. In accordance with their location, adatoms can be subdivided into edge and corner adatoms [Fig. 1(b)]. The Al-modified Si(111)7 × 7 (labeled also as Si(111)α-7 × 7-Al phase³⁻⁶) has been recognized to be essentially an ordered array of surface magic clusters, where each cluster is built of six Al atoms and three Si atoms⁷⁻⁹ [Fig. 1(c)]. Under proper preparation, magic clusters occupy every 7 × 7 half unit cell. The number of dangling-bond atoms in the α-7 × 7 phase is significantly reduced. As the magic cluster is free of dangling bonds, only three corner adatoms preserve their dangling bonds in the 7 × 7 HUC. In turn, the electronic state and reactivity of these corner adatoms are affected by the formed magic clusters through a charge transfer.¹⁰ There are numerous papers on the C₆₀ adsorption onto Si(111)7 × 7 surface,¹¹⁻¹⁸ and a few for the case of C₇₀.^{19,20} To our knowledge, the Si(111)α-7 × 7-Al surface has never been tested as a substrate for fullerene adsorption.

Third, besides the room-temperature (RT) adsorption (which were explored in the most previous works), fullerene adsorption at higher temperatures, 450 and 600 K, has also been examined in the present work. Note that these temperatures are still well below the threshold of fullerene decomposition and

^{a)}Electronic mail: zotov@iacp.dvo.ru

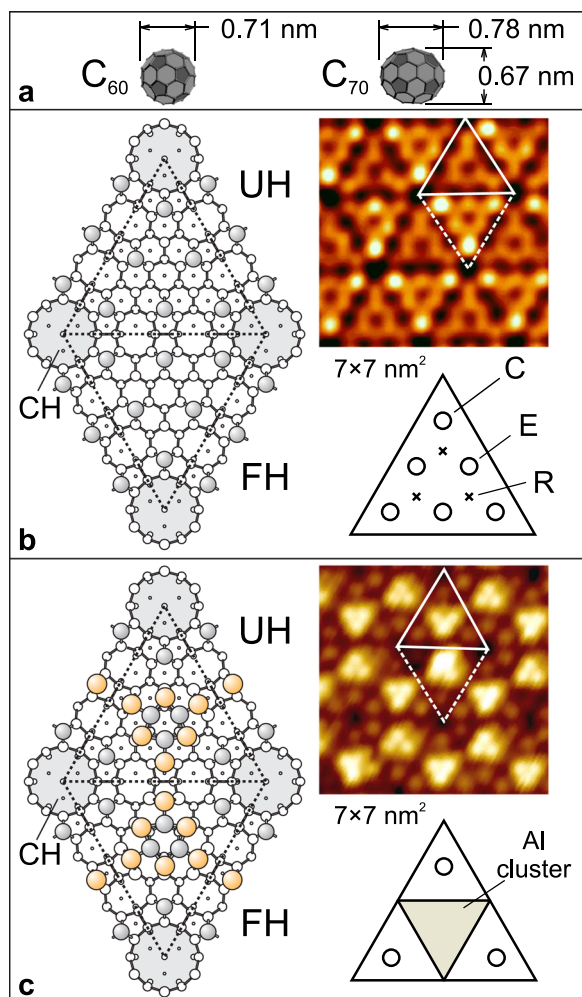


FIG. 1. (Color online) Schematic models of (a) C₆₀ and C₇₀ fullerenes, (b) Si(111)7×7 reconstruction, and (c) Al magic clusters (α -7×7-Al reconstruction). For the reconstructions, both STM images (7×7 nm²) and simplified sketches are provided. Corner adatoms, edge adatoms, and rest atoms are labeled by corresponding initial letters. “CH” marks the corner hole.

SiC formation.^{12,19} These observations are expected to provide a hint for elucidating the role of kinetic limitations in the fullerene adsorption phenomena.

II. EXPERIMENT

Experiments were carried out in the ultrahigh vacuum Omicron MULTIPROBE system with a base pressure better than 2×10^{-10} Torr. Atomically clean Si(111)7×7 surfaces were prepared *in situ* by flash-annealing process at 1280 °C after the samples were first outgassed at 600 °C for several hours. Si(111) α -7×7-Al surfaces were prepared by depositing ~ 0.25 ML Al [one monolayer (ML) = 7.8×10^{14} cm⁻²] from Al-wrapped W wire onto Si(111)7×7 surface held at 550 °C. Fullerenes, C₆₀ (Alfa Aesar, purity 99.92%) and C₇₀ (BuckyUSA, purity 99.5%), were deposited from resistively heated Mo boats. The typical fullerene dose was ~ 0.0015 ML. STM images were acquired using Omicron variable-temperature STM VT-XA operating in a constant-current mode. For STM experiments, mechanically cut PtIr tips

cleaned by *in situ* heating were used. All STM observations were performed at RT.

III. RESULTS AND DISCUSSION

At a glance, C₆₀ and C₇₀ demonstrate similar general behavior on both pristine Si(111)7×7 and Si(111) α -7×7-Al surfaces. As an example, this is illustrated by Fig. 2 showing a set of STM images obtained after C₇₀ fullerene adsorption onto the Si(111) α -7×7-Al (hereafter α -Al for short) at 300, 450, and 600 K. At RT, fullerenes are scattered on the surface preferably as isolated molecules; formation of dimers is observed rather seldom at this coverage. At about 450 K [Fig. 2(b)], as a result of growing mobility of fullerenes, the fraction of molecules arranged in dimers sufficiently increases up to ~ 0.4 . Spacings between molecules are 1.00 ± 0.01 nm and 1.10 ± 0.03 nm for C₆₀-C₆₀ and C₇₀-C₇₀ pairs, respectively, which is quite close to corresponding lattice parameters of the bulk fullerites. At even higher temperature, about 600 K, the fullerene mobility is high enough that both C₆₀ and C₇₀ start to form small patches of close-packed array [Fig. 2(c)]. In all the cases considered here, intramolecular features have been clearly observed [Fig. 2(d)], indicating that the fullerenes are fixed (not rotated) due to a strong bonding to a surface. These STM features are consistent in general with the previously published results on fullerenes adsorbed onto the silicon surfaces.^{14,17,20} It is worth noting, however, that the fullerenes are oriented randomly without any apparent ordering or preference for the selected orientations.

Fullerene positions were determined using corner holes of the 7×7 lattice as reference points. For each case, location of 300–500 fullerenes was fixed to get a reliable statistics. Figure 3 shows two selected examples of raw data, namely, C₆₀/7×7 and C₆₀/ α -Al at RT. Each red cross indicates the position of a fullerene center. Taking into account the symmetry of the 7×7 unit cell, the data were folded to minimize the number of apparent adsorption sites. Thus, one can see that primary adsorption sites for C₆₀ on 7×7 surface are directly above a rest atom (i.e., the “threefold position”) and above a corner hole in agreement with the results of the recent study.¹⁸ Although a certain difference between faulted

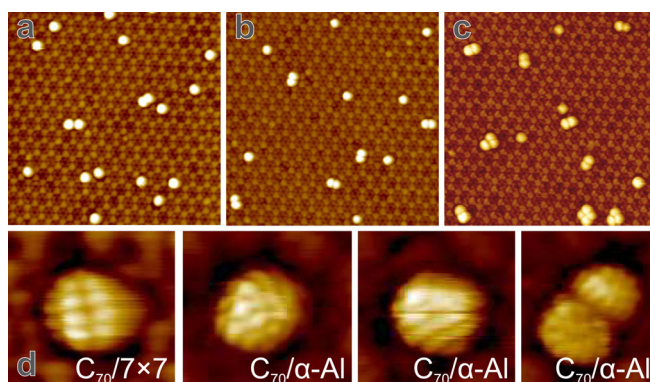


FIG. 2. (Color online) STM images of 40×40 nm² of C₇₀ adsorbed onto Si(111) α -7×7-Al surface at (a) 300 K, (b) 450 K, and (c) 600 K. (d) Selection of STM images of fullerenes displaying the intramolecular contrast.

and unfaulted HUCs was detected (with preference ratio of $\sim 4:3$ for the faulted HUC), this does not seem very crucial, and for the sake of simplicity, we merged the halves together. For the case of C₆₀ and C₇₀ on α -Al, the similar processing procedure was applied [Fig. 3(b)]. Finally, the symmetrized data sets were used to construct the 2D histograms (Fig. 4), which summarize adsorption sites with respect to a half unit cell (bin size = 0.125×0.125 nm²).

As mentioned above, the most abundant adsorption site ($\sim 95\%$ occupation) for both C₆₀ and C₇₀ on the pristine 7×7 surface at RT is almost above a rest atom between three adatoms, two edge ones, and one corner. {Although the whole data set is apparently centered at the rest atom, distribution of the distances measured from the rest atom to the center of an individual fullerene has a maximum at about 0.2 nm [Fig. 6(a)].} The next favorable position is above a corner hole ($\sim 5\%$ occupation). Remarkably, the center of the unit cell, which is also located between three adatoms but without the rest atom underneath, almost never hosts the fullerene in contrast to early STM studies.¹¹ Nevertheless, this result agrees with the more recent AFM study.¹⁸ At slightly elevated temperature, 450 K, the preferable position changes to the site located almost directly above the edge adatom. Changing the preferable position with increasing temperature implies that a new site is characterized by a deeper potential minimum but fullerene has to surmount a certain barrier to reach this site. A reasonable guess is that C₆₀ might displace Si adatoms to adopt a stable binding with the rest Si layer where three new dangling bonds appeared due to removing adatom. One can see a certain analogy with adsorption behavior of fullerenes on metal surfaces where fullerene displaces metal atoms and creates a nanopit to enhance bonding energy with a substrate.^{21–31} Apparent heights of C₆₀ residing in the rest-atom sites and adatom sites appear to be similar, which sounds supportive for the suggestion of the adatom removal since in both cases C₆₀ would reside on the Si rest-atom layer.

Worth noting that similar positions on adatom sites were observed previously in the case of RT submonolayer C₆₀ deposition onto the 7×7 surface.³² However, discrepancy in determination of the bonding sites at the 7×7 surface was

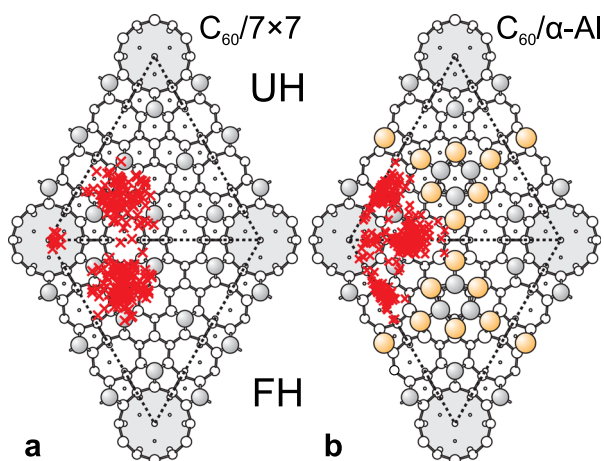


FIG. 3. (Color online) Examples of symmetrized data sets for C₆₀ fullerene adsorption on (a) Si(111) 7×7 and (b) α -Al surfaces.

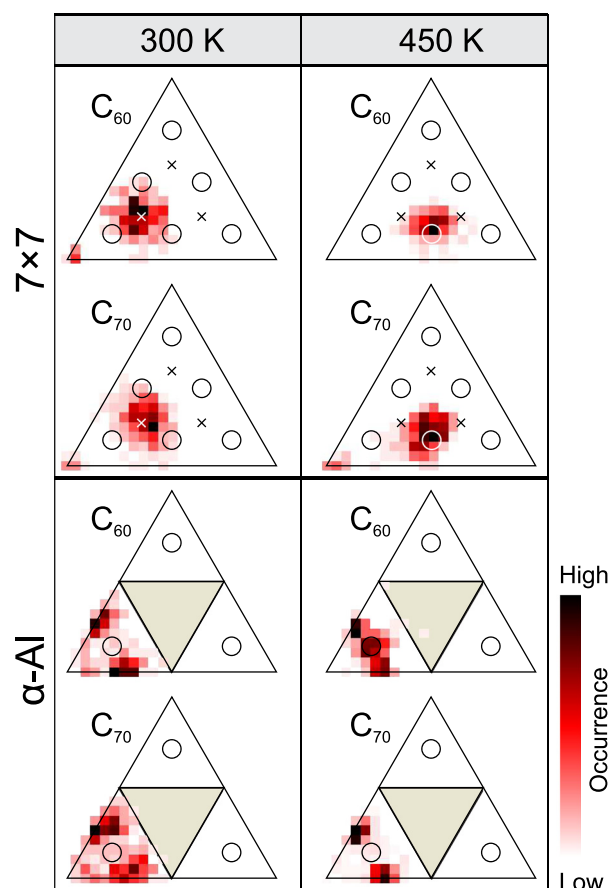


FIG. 4. (Color online) Distribution (2D histogram) of fullerene adsorption sites superposed on the corresponding 7×7 HUCs.

noticed long ago, and Moriarty¹⁶ argued that this may be connected to the details of the sample preparation and accuracy in determination of C₆₀ locations. Nevertheless, a tendency for C₆₀ and C₇₀ to occupy the edge-adatom site seems obvious.

The occurrence of Al magic cluster in the α -Al phase inside the 7×7 unit cell makes the edge adatoms unavailable for fullerene adsorption. In this situation, one might expect that fullerenes would occupy the second preferable bonding site, a corner hole. However, the number of molecules in this site is even less than at the pristine 7×7 surface. The most stable position now was determined to be the one above the dimer row, a border between the faulted and unfaulted 7×7 HUCs.

This position is highly asymmetric (Fig. 5) which is not typical for isolated fullerenes considering the strong bonding to the surface (otherwise they would form compact 2D islands). However, one may notice that the lateral distance from this position to the nearest adatom {ideally 0.37; 0.35 and 0.36 nm—measured values for C₆₀ and C₇₀, respectively [Fig. 6(b)]} is rather close to that between adatoms and the rest atom (0.44 nm). Taking into account that fullerenes rarely sit directly over rest atoms [see Fig. 6(a)], one may conclude that after edge adatoms were blocked by Al, fullerenes prefer to keep the same distance to a dangling bond (i.e., adatom) rather than having a more symmetric position (e.g., at a corner hole).

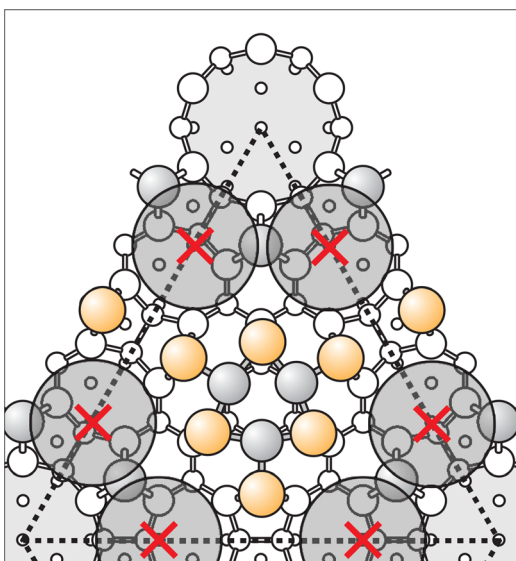


Fig. 5. (Color online) Average adsorption positions for both C₆₀ and C₇₀ on the α -Al surfaces.

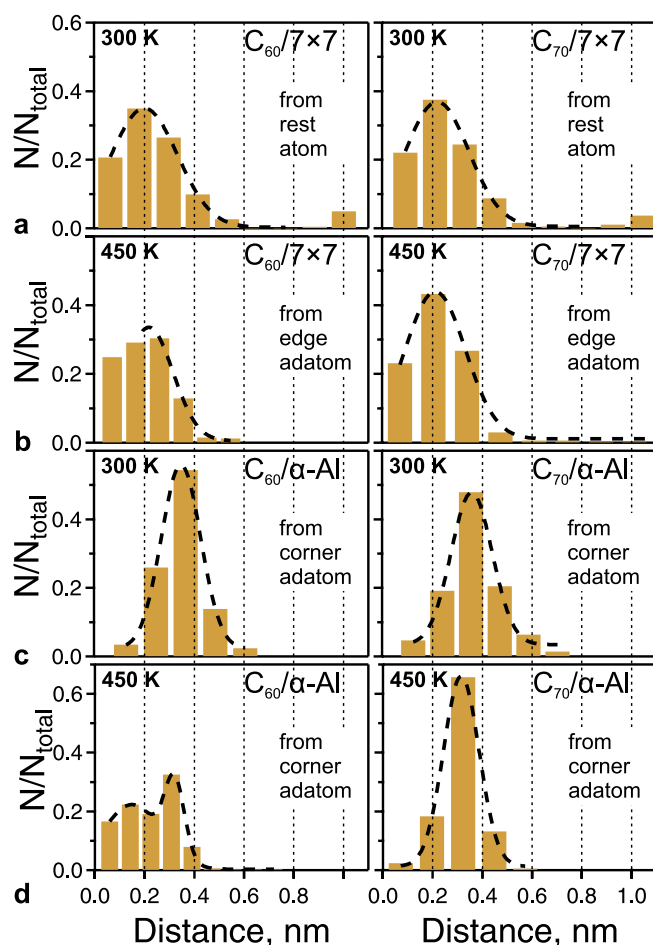


Fig. 6. (Color online) Distributions of spacings between fullerene centers and (a) the rest atom of the 7×7 reconstruction at 300 K, (b) the edge adatom of the 7×7 reconstruction at 450 K, (c) the corner adatom of the α -Al surface at 300 K, and (d) the corner adatom of the α -Al surface at 450 K.

Increasing the growth temperature to 450 K produces modest effect on the characteristics of the C₇₀/ α -Al system: the C₇₀ fullerenes still prefer to occupy the same position at a dimer row (Fig. 4, bottom row), but the spacing distribution becomes sharper [Fig. 6(c)]. In the case of the C₆₀/ α -Al system, the changes appear to be more pronounced. Though about a half of the C₆₀ fullerenes preserves their original RT-position at a dimer row, the other half begins to occupy a new position inside the 7×7 unit cell, namely, almost directly over corner adatom (see Fig. 4, the second row from bottom). This is reflected by the two-maxima shape of the corresponding spacing distribution [Fig. 6(d)]. Note that such a change of a location for the adatom site at increased temperature is reminiscent for the C₆₀ behavior on Si(111) 7×7 surface at 450 °C (Fig. 4, top row) and in both cases Si adatom is plausibly displaced by C₆₀ fullerene. In general, one can conclude that type of fullerenes and their surface environment might affect fullerene adsorption behavior in a rather complicated way.

As a final remark, we would like to compare the present STM observations on C₆₀ adsorption onto Si(111) 7×7 surface with the results of the recent theoretical calculations by Ruruli *et al.*¹⁵ The experiment and calculations coincide in a strong preference for C₆₀ occupying the rest-atom site rather than the center of HUC surrounded by the edge adatoms. However, many other items are in variance. Calculations predict the corner hole to be the most preferable adsorption site. The present experiment shows that only 5% of fullerenes reside in corner holes at RT and their fraction even decreases at 450 K. Theoretical results suggest that unfaulted HUCs are more preferable than faulted HUCs. Experiment reveals an opposite behavior: fullerenes prefer faulted HUCs rather than unfaulted HUCs. In addition, C₆₀ residence at the edge adatom site (with possible removing of the adatom) detected at 450 K was not considered in the theoretical work. The C₇₀ fullerenes and Si(111) α - 7×7 -Al as a hosting surface are also awaiting for the theoretical consideration.

IV. CONCLUSIONS

In conclusion, preferable adsorption sites of C₆₀ and C₇₀ fullerenes on pristine and Si(111) 7×7 and Si(111) α - 7×7 -Al were determined using statistical analysis of the STM images acquired at very early stages of fullerene adsorption. It was found that both C₆₀ and C₇₀ prefer to occupy positions above the Si rest atoms upon adsorption onto Si(111) 7×7 at 300 K and change their preferable sites for those located at the Si edge adatom at 450 K. Occupation of these sites is plausibly accompanied by releasing the Si adatom. Upon C₆₀ and C₇₀ adsorption onto Si(111) α - 7×7 -Al surface at 300 K, the fullerenes prefer to occupy the asymmetric sites at the dimer rows, the borders of the 7×7 unit cell halves. At 450 K, the C₇₀ fullerenes preserve this location, while about half of the C₆₀ fullerenes changes it for that at the corner Si adatom position with plausible removal of the adatom. Taking into account that atomic arrangement of Si(111) 7×7 and Al-modified Si(111) α - 7×7 -Al is understood in detail, the present experimental data set can serve a useful basis for

theoretical analysis both from the viewpoint of understanding the fullerene adsorption behavior on these surfaces as well as for testing validity and accuracy of calculations.

ACKNOWLEDGMENT

The work was supported by Russian Science Foundation under Grant No. 14-12-00482.

- ¹H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature* **318**, 162 (1985).
- ²K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, *J. Vac. Sci. Technol., A* **3**, 1502 (1985).
- ³J. J. Lander and J. Morrison, *J. Appl. Phys.* **36**, 1706 (1965).
- ⁴K. Nishikata, K. Murakami, M. Yoshimura, and A. Kawazu, *Surf. Sci.* **269/270**, 995 (1992).
- ⁵M. Yoshimura, K. Takaoka, T. Yao, T. Sato, T. Sueyoshi, and M. Iwatsuki, *Phys. Rev. B* **47**, 13930 (1993).
- ⁶E. A. Khramtsova, A. V. Zotov, A. A. Saranin, S. V. Ryzhkov, A. B. Chub, and V. G. Lifshits, *Appl. Surf. Sci.* **82/83**, 576 (1994).
- ⁷J. Jia, J. Z. Wang, X. Liu, Q. K. Xue, Z. Q. Li, Y. Kawazoe, and S. B. Zhang, *Appl. Phys. Lett.* **80**, 3186 (2002).
- ⁸V. G. Kotlyar, A. V. Zotov, A. A. Saranin, T. V. Kasyanova, M. A. Cherevik, I. V. Pisarenko, and V. G. Lifshits, *Phys. Rev. B* **66**, 165401 (2002).
- ⁹J. F. Jia, X. Liu, J. Z. Wang, J. L. Li, X. S. Wang, Q. K. Xue, Z. Q. Li, Z. Zhang, and S. B. Zhang, *Phys. Rev. B* **66**, 165412 (2002).
- ¹⁰M. Franz, J. Schmermbeck, and M. Dähne, *J. Vac. Sci. Technol., B* **34**, 04J101 (2016).
- ¹¹X. D. Wang, T. Hashizume, H. Shinohara, Y. Saito, Y. Nishina, and T. Sakurai, *Jpn. J. Appl. Phys., Part 2* **31**, L983 (1992).
- ¹²D. Chen, R. K. Workman, and D. Sarid, *J. Vac. Sci. Technol., B* **14**, 979 (1996).
- ¹³J. G. Hou, J. Yang, H. Wang, Q. Li, C. Zeng, H. Lin, B. Wang, and D. M. Z. Q. Chen, *Phys. Rev. Lett.* **83**, 3001 (1999).
- ¹⁴C. P. Huang, C. C. Su, and M. S. Ho, *Appl. Surf. Sci.* **254**, 7712 (2008).
- ¹⁵R. Rurali, R. Cuadrado, and J. I. Cerdá, *Phys. Rev. B* **81**, 075419 (2010).
- ¹⁶P. J. Moriarty, *Surf. Sci. Rep.* **65**, 175 (2010).
- ¹⁷X. Du, F. Chen, X. Cen, X. Wu, Y. Cai, X. Liu, and L. Wang, *Appl. Phys. Lett.* **97**, 253106 (2010).
- ¹⁸S. I. Kobayashi and Y. Cho, *Surf. Sci.* **606**, 174 (2012).
- ¹⁹T. Wakita, K. Sakamoto, A. Kasuya, Y. Nishina, and S. Suto, *Appl. Surf. Sci.* **144/145**, 653 (1999).
- ²⁰G. Lee, H. Shim, and J. Woo, *J. Korean Phys. Soc.* **55**, 1707 (2009).
- ²¹J. A. Gardener, G. A. D. Briggs, and M. R. Castell, *Phys. Rev. B* **80**, 235434 (2009).
- ²²L. Tang, X. Zhang, Q. Guo, Y.-N. Wu, L.-L. Wang, and H.-P. Cheng, *Phys. Rev. B* **82**, 125414 (2010).
- ²³X. Q. Shi, A. B. Pang, K. L. Man, R. Q. Zhang, C. Minot, M. S. Altman, and M. A. Van Hove, *Phys. Rev. B* **84**, 235406 (2011).
- ²⁴C. Liu, Z. Qin, J. Chen, Q. Guo, Y. Yu, and G. Cao, *J. Chem. Phys.* **134**, 044707 (2011).
- ²⁵X. Torrelles, V. Langlais, M. D. Santis, H. C. N. Tolentino, and Y. Gauthier, *Phys. Rev. B* **81**, 041404 (2010).
- ²⁶X. Torrelles, M. Pedio, C. Cepek, and R. Felici, *Phys. Rev. B* **86**, 075461 (2012).
- ²⁷H. I. Li *et al.*, *Phys. Rev. Lett.* **103**, 056101 (2009).
- ²⁸W. W. Pai *et al.*, *Phys. Rev. Lett.* **104**, 036103 (2010).
- ²⁹K. Pussi *et al.*, *Phys. Rev. B* **86**, 205406 (2012).
- ³⁰G. Xu, X.-Q. Shi, R. Q. Zhang, W. W. Pai, H. T. Jeng, and M. A. Van Hove, *Phys. Rev. B* **86**, 075419 (2012).
- ³¹H. Shin *et al.*, *Phys. Rev. B* **89**, 245428 (2014).
- ³²D. Chen, J. Chen, and D. Sarid, *Phys. Rev. B* **50**, 10905 (1994).