



Self-assembled C₆₀ layers on incommensurate Cu/Si(111)'pseudo-5 × 5' surface



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ARTICLE INFO

Article history:

Received 15 June 2015

Accepted 31 July 2015

Available online 5 August 2015

Keywords:

Atom–solid interactions

Silicon

Fullerene

Self-assembly

Scanning tunneling microscopy

ABSTRACT

Self-assembled growth of C₆₀ monolayers on the pristine and Ge-modified Cu/Si(111)'pseudo-5 × 5' surfaces was studied using scanning tunneling microscopy observations. The pristine Cu/Si(111)'pseudo-5 × 5' surface shows up as an incommensurate reconstruction on Si(111) substrate, while Ge-modified surface shows up as an array of Ge atomic clusters grown on the Cu/Si(111)'pseudo-5 × 5' template. It has been found that C₆₀ fullerenes are highly mobile on the both surfaces, hence at the early growth stages fullerenes are accumulated along the atomic steps forming their quasi-one-dimensional molecular stripes. With further C₆₀ deposition, almost ideal two-dimensional close-packed molecular monolayers are formed. The layers are modulated as evidenced by developing quasi-periodic pattern of dim and bright fullerenes displaying 2 × 2 periodicity. Contrast difference between dim and bright fullerenes is supposed to have a topographical origin, namely, bright fullerenes reside higher than dim fullerenes. Dim fullerenes were concluded to occupy centers of hexagons which constitute honeycomb-like structure of the Cu/Si(111)'pseudo-5 × 5' surface. For the Ge-modified surface, this means that adsorbing C₆₀ fullerenes displace Ge atoms from their original positions to the interstitial sites in the molecular monolayer. Ge atoms were found to terminate rotational motion of selected fullerenes in the layer.

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1. Introduction

Interaction of fullerenes with reconstructed crystalline surfaces has been found to present a number of fascinating phenomena both at the initial stage of molecular island nucleation and growth as well as at the final stage of monomolecular layer completion followed by multi-layer growth. Some of these phenomena are related to diversity of the adsorption sites which fullerenes can occupy on the reconstructed surface. At the stage of island growth, difference in C₆₀ adsorption energy for different sites can be utilized to improve spatial ordering of the molecular islands [1–4] and to sharpen their size distribution [1,5]. When extended C₆₀ arrays are formed, difference in C₆₀ adsorption geometries leads to developing modulations in the molecular layers which typically appear as regular occurrence of fullerenes displaying different contrast, bright and dim, in scanning tunneling microscopy (STM) images [6–14]. Incommensurate surfaces constitute an interesting class of reconstructed surfaces [15]. Such surfaces are typically characterized by a quasi-periodic domain structure associated with strain-relief pattern. Starting from the seminal work on the growth of Ag and Cu layers on Pt(111)

[16], self-assembly of atoms [17] and molecules, in particular C₆₀ fullerenes [3,18], on the incommensurate surfaces has become an advanced topic in surface science.

Cu/Si(111)'pseudo-5 × 5' reconstruction presents a vivid example of the incommensurate surface. The surface shows up as a honeycomb-like array formed by domain-boundary network with domains having a shape of non-regular hexagons. The hexagon sizes are close (but not identical), being ~5.5a₀ in average. The latter coins the 'pseudo-5 × 5' notation of the reconstruction to underline its quasi-periodic arrangement. [a₀ = 3.84 Å, the lattice constant of the non-reconstructed Si(111)1 × 1 surface.] The 5.5a₀ = 21.12 Å, that is close to the doubled C₆₀–C₆₀ distance (~20 Å) in the bulk fullerite and monomolecular close-packed C₆₀ arrays on the surfaces. Thus, the surface seems to be a promising template for growing ordered C₆₀ layers. As shown in Ref. [17], upon room temperature (RT) adsorption of ~0.1 ML (1 monolayer (ML) = 7.8 × 10¹⁴ cm⁻²) of Ge, the Cu/Si(111)'pseudo-5 × 5' reconstruction is preserved, while Ge atoms form an ordered array of atomic clusters. Thus, Ge-modified Cu/Si(111)'pseudo-5 × 5' surface can be thought as a template having the same periodicity as the parent surface but different chemical and topographic properties.

In the present work, using scanning tunneling microscopy (STM) observations we have explored self-assembly of C₆₀ layers on the pristine and Ge-modified incommensurate Cu/Si(111)'pseudo-5 × 5' surfaces.

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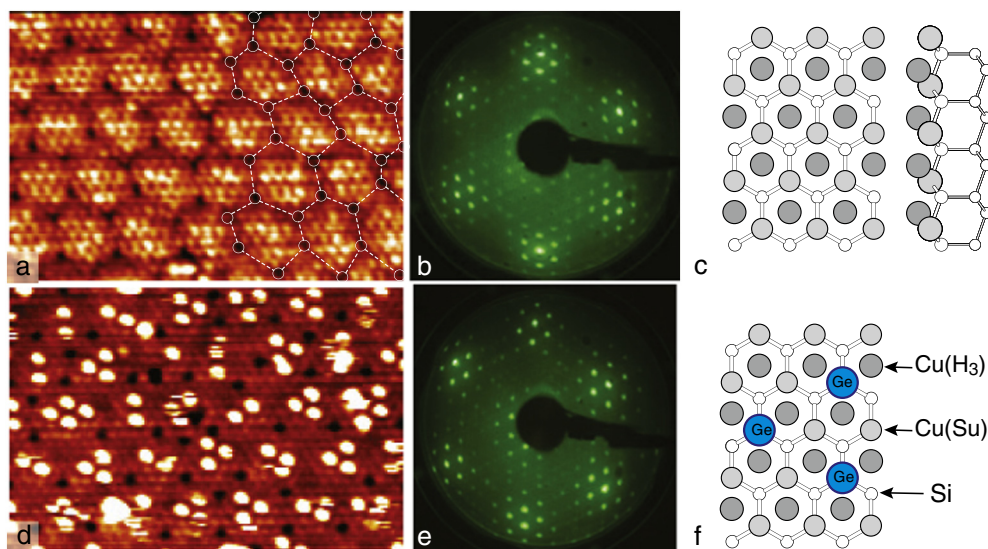


Fig. 1. STM images (scale: $150 \times 100 \text{ \AA}^2$) and LEED patterns ($E_p = 40\text{eV}$) of (a, b) pristine Si(111)'pseudo- 5×5 -Cu surface and (d, e) Si(111)'pseudo- 5×5 -Cu surface with adsorbed 0.1 ML Ge. In the right half of (a), boundaries of the hexagonal domains are outlined by dashed lines and crater defects are marked by open circles. Schematic diagrams illustrating atomic structure of the (c) pristine Si(111)'pseudo- 5×5 -Cu surface and (f) Si(111)'pseudo- 5×5 -Cu surface with adsorbed Ge atoms. Cu(Su) and Cu(H₃) atoms are shown by light gray and dark gray circles, respectively, Si atoms by white circles and Ge atoms by blue circles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Experimental details

Our experiments were performed with an Omicron VT-STM operating in an ultrahigh vacuum ($\sim 2.0 \times 10^{-10}$ Torr). Atomically-clean Si(111) 7×7 surfaces were prepared *in situ* by flashing to 1280 °C after the samples were first outgassed at 600 °C for several hours. Copper and germanium were deposited from W filaments and C₆₀ fullerenes from a Ta boat. In order to form the Si(111)'pseudo- 5×5 -Cu surface, 2.0 ML of Cu was deposited onto the Si(111) 7×7 surface held at RT followed by

brief (~ 15 s) annealing with DC current at 600 °C. For STM observations, electrochemically etched tungsten tips cleaned by *in situ* heating were employed.

3. Results and discussion

Fig. 1a and b show STM images of the pristine and Ge-adsorbed Si(111)'pseudo- 5×5 -Cu surfaces, respectively. In agreement with the reported STM observations [19–22], at a large scale the Si(111)'pseudo-

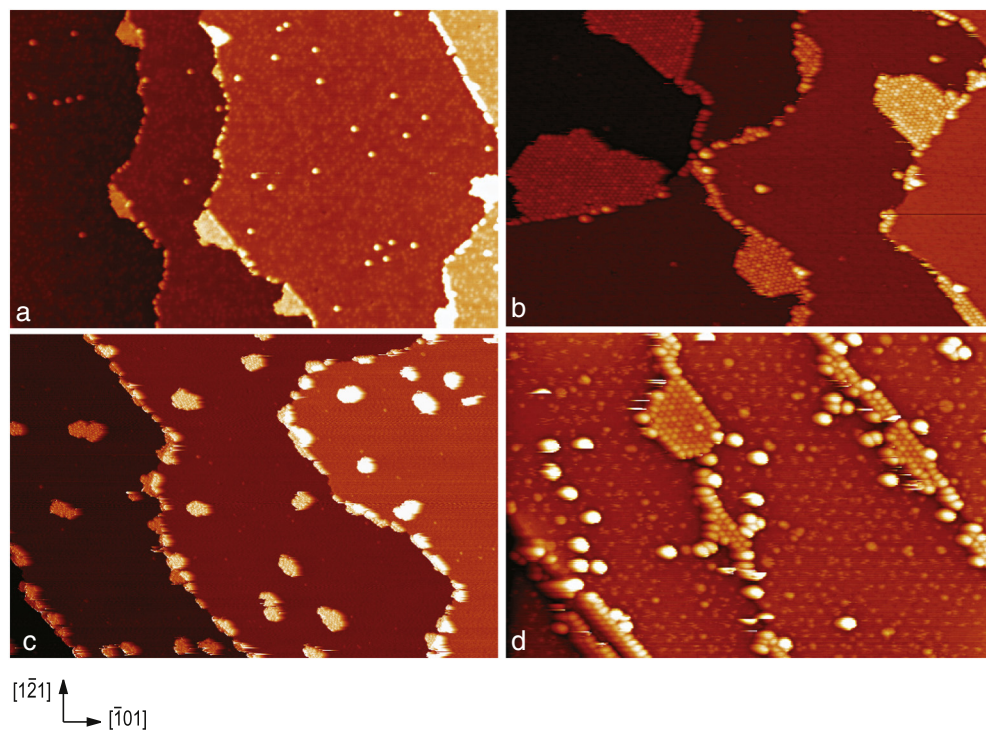


Fig. 2. STM images illustrating early stages of C₆₀ layer growth. Si(111)'pseudo- 5×5 -Cu surface after RT adsorption of (a) $\sim 5\%$ and (b) $\sim 10\%$ of C₆₀ monomolecular layer. (c) Si(111)'pseudo- 5×5 -Cu surface after adsorption of $\sim 10\%$ of C₆₀ monomolecular layer at 110 K. (d) Ge-adsorbed Si(111)'pseudo- 5×5 -Cu surface after RT adsorption of $\sim 10\%$ C₆₀ monomolecular layer. Scale: (a) $1900 \times 1300 \text{ \AA}^2$; (b) and (c) $1000 \times 670 \text{ \AA}^2$; (d) $750 \times 500 \text{ \AA}^2$.

5×5 -Cu surface shows up as a honeycomb-like array formed by the quasi-regular domain-boundary network, while at the atomic scale its characteristic features are the 1×1 -like structure in the interior of the domains and the presence of the vacancy-like crater defects. Domains have a shape of non-regular hexagons with crater defects in the corners (Fig. 1a). For the local atomic arrangement of the 1×1 structure at the 'pseudo- 5×5 -Cu/Si(111) interface, the Cu_2Si model [23] has recently been accepted by most of the researchers [17,22–26]. According to the model, Cu_2Si -layer structure is composed of 1 ML Cu adsorbed in H_3 sites (denoted as $\text{Cu}(\text{H}_3)$ atoms in Fig. 1f) and 1 ML Cu substituting for Si in the upper half of the Si(111) double layer (denoted as $\text{Cu}(\text{Su})$ in Fig. 1f). The round protrusions seen in the filled-state STM images were proved to be associated with the $\text{Cu}(\text{H}_3)$ atoms [17].

In the case of Ge adsorption, the Si(111)'pseudo- 5×5 -Cu surface has been found to show up as an array of the attraction basins associated with its quasi-periodic domain structure [17]. As a result, Ge atoms are trapped inside hexagonal domains. At relatively low Ge coverages (e.g., ~ 0.03 ML), single Ge atom remains highly mobile within a given domain at RT, but at a coverage of ~ 0.1 ML, Ge atoms agglomerate into the stable atomic clusters, among which trimers are the most abundant species (Fig. 1d). Within the cluster, Ge atoms were found to occupy the sites above $\text{Cu}(\text{Su})$ atoms [17] (Fig. 1f).

Fig. 2 shows the pristine and Ge-adsorbed Si(111)'pseudo- 5×5 -Cu surfaces after RT and low-temperature (110 K) adsorption of relatively small amounts of C_{60} (about 5 and 10% of the C_{60} monomolecular layer). Principal regularities of the early stages of C_{60} layer growth on both template surfaces appear to be similar. Namely, almost all deposited fullerenes are accumulated along the surface step edges except for the rare C_{60} fullerenes left at the terraces. Density of such fullerenes

(which are plausibly trapped by surface defects) is slightly higher for the Ge-modified surface, however their fraction is still minor. If the sample was held at low temperature of 110 K during C_{60} deposition, the defect-trapped C_{60} fullerenes act as nuclei for the C_{60} islands forming at terraces (Fig. 2c). Thus, one can conclude that C_{60} are highly mobile on both surfaces and attractive basins at the surface potential relief (which control effectively Ge clustering) appear to be very shallow for C_{60} fullerenes and do not affect noticeably their migration, at least, down to 110 K. In other words, at the early stage of C_{60} layer growth atomic-scale structure of the pristine and Ge-adsorbed Si(111)'pseudo- 5×5 -Cu surfaces does not demonstrate any template effect. Note that this is contrasted to the C_{60} growth on the incommensurate Ag/Pt(111) surface where C_{60} island nucleation is dictated by surface potential relief [3,18].

With further C_{60} deposition, the close-packed C_{60} arrays grow in size and eventually all the surface area becomes occupied by monomolecular C_{60} layer (Fig. 3a). Remarkably, the growth of the second layer starts only when more than ~ 90 – 95% of the surface has already been covered by the first monomolecular layer. Thus, the Si(111)'pseudo- 5×5 -appropriate amount of C_{60} . This is a characteristic feature of both pristine and Ge-adsorbed Si(111)'pseudo- 5×5 -Cu surfaces.

Another common feature of C_{60} monolayers on the two surfaces is a presence of spatial modulations within the layers as highlighted by occurrence of fullerenes having different STM contrast, bright and dim (Fig. 4a and c). Note that the second C_{60} monolayer is, in contrast, quite homogeneous with all fullerenes displaying the same contrast (Fig. 3b). In the first monolayer, the dim and bright fullerenes form a quasi-periodic structure with a 2×2 periodicity which is more clearly seen in the FFT patterns taken from the STM images (Fig. 4b). Note that developing of the 2×2 superstructure is quite expected due an approximate resemblance of the $5.5a_0$ substrate periodicity and the doubled C_{60} – C_{60} intermolecular distance, as mentioned above. This resemblance can be visualized also by the coincidence of sizes of

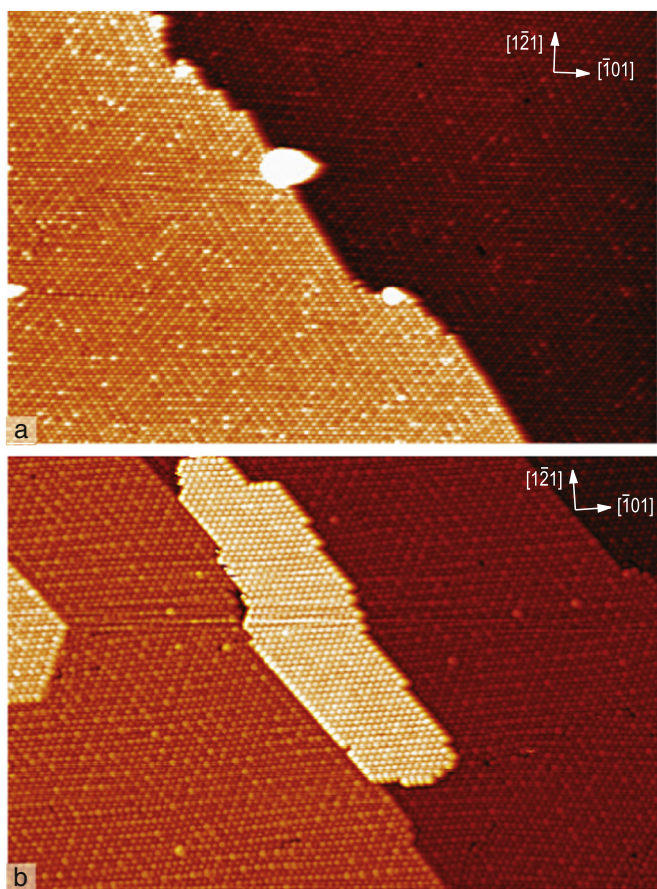


Fig. 3. (a) $1000 \times 670 \text{ \AA}^2$ STM image of the completed C_{60} monomolecular layer. (b) $1000 \times 670 \text{ \AA}^2$ STM image illustrating nucleation of the second-layer C_{60} island near the step edge.

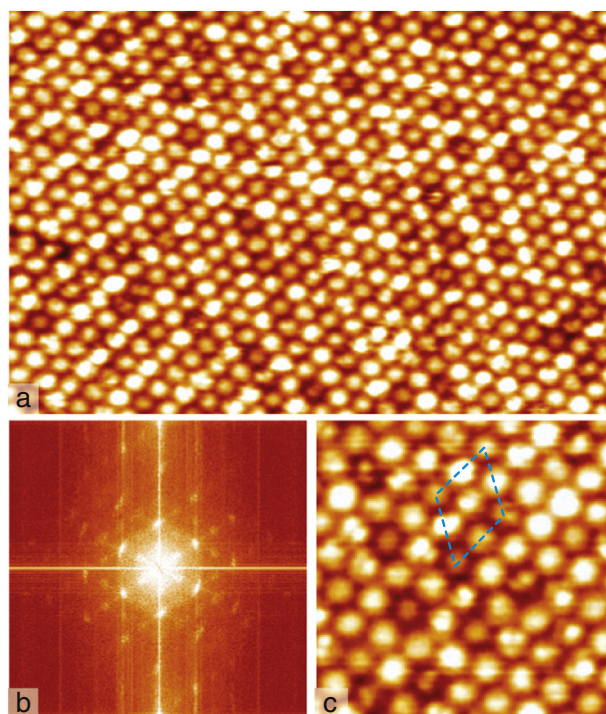


Fig. 4. (a) 280×200 and (b) $85 \times 85 \text{ \AA}^2$ STM images and (c) corresponding FFT image illustrating developing quasi-periodic 2×2 pattern of the dim and bright fullerenes in the monomolecular C_{60} layer. The 2×2 unit cell is outlined by blue dashed frame. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

seven-molecule hexagonal cluster and hexagonal domain of the Si(111)'pseudo- 5×5 -Cu surface reconstruction. Thus, the 2×2 periodicity arises since the fullerene in the cluster center displays a brightness different from that of the six surrounding fullerenes residing along the hexagon boundaries. This is illustrated in the schematic diagram in Fig. 5b. Comparing this scheme with real STM images, one can see that the main surface motif is associated with the dim fullerenes surrounded by the bright fullerenes (i.e., the dark fullerene is in the hexagon center, while bright fullerenes are along its sides). If the surface would have a strictly-periodic 2×2 structure, the ratio of dim-to-bright C_{60} molecules would be 1:3. Though the long-range 2×2 ordering is lacking as a natural consequence of the quasi-periodic incommensurate structure of the underlying substrate surface, estimation for the real surface also demonstrates that dim fullerenes constitute about 25% of all fullerenes. Fig. 5a shows a schematic of the quasi-periodic 2×2 structure where fullerenes residing close to the hexagon centers are shown by dark brown circles, those residing close to the domain boundaries and at the domain boundaries by orange and yellow circles, respectively.

It is worth noting that developing of the 2×2 periodicity has also been reported to take place at the surface of multi-layer C_{60} films upon cooling to low temperatures [27–29]. Though the physical origin of the 2×2 superstructures in the two cases is quite different: at the multi-layer surface it is associated with the spatial ordering of molecules having two different orientations (hexagon-up and tilted), in the

present case it is controlled by the difference of C_{60} films upon cooling to low temperature adsorption state in the center and at the periphery of the hexagonal domain of the 'pseudo- 5×5 ' Cu/Si(111) reconstruction. The common feature is that the both reconstructions are effectively described by a seven-molecular hexagonal cluster where the central molecule differs in properties from those surrounding it.

An important question concerns the origin of the difference in the STM contrast of dim and bright fullerenes which can be governed either by topography or by electronic effects. In order to resolve the question, we conducted STM observations at various bias voltages and measured the height difference Δh as a function of bias. Fig. 6 shows the plot of this dependence. Note that absence of data in the bias range from -1.0 V to $+1.0$ V is due to the energy gap between HOMO and LUMO orbitals of C_{60} fullerenes. One can see in Fig. 6 that at both polarities the dim/bright height difference remains essentially constant being ~ 0.4 – 0.5 Å. This result indicates that topography effect prevails and C_{60} molecules in the centers of the 'pseudo- 5×5 ' hexagons just sit lower than fullerenes located at the periphery of hexagons. However, bearing in mind slight difference between Δh values obtained for negative and positive biases as well as noticeable scatter of the data possible electronic effects cannot be completely excluded.

Remarkably, dim/bright fullerene pattern on the Ge-modified Si(111)'pseudo- 5×5 -Cu surface is similar to that on the pristine Si(111)'pseudo- 5×5 -Cu surface. However, one would expect an

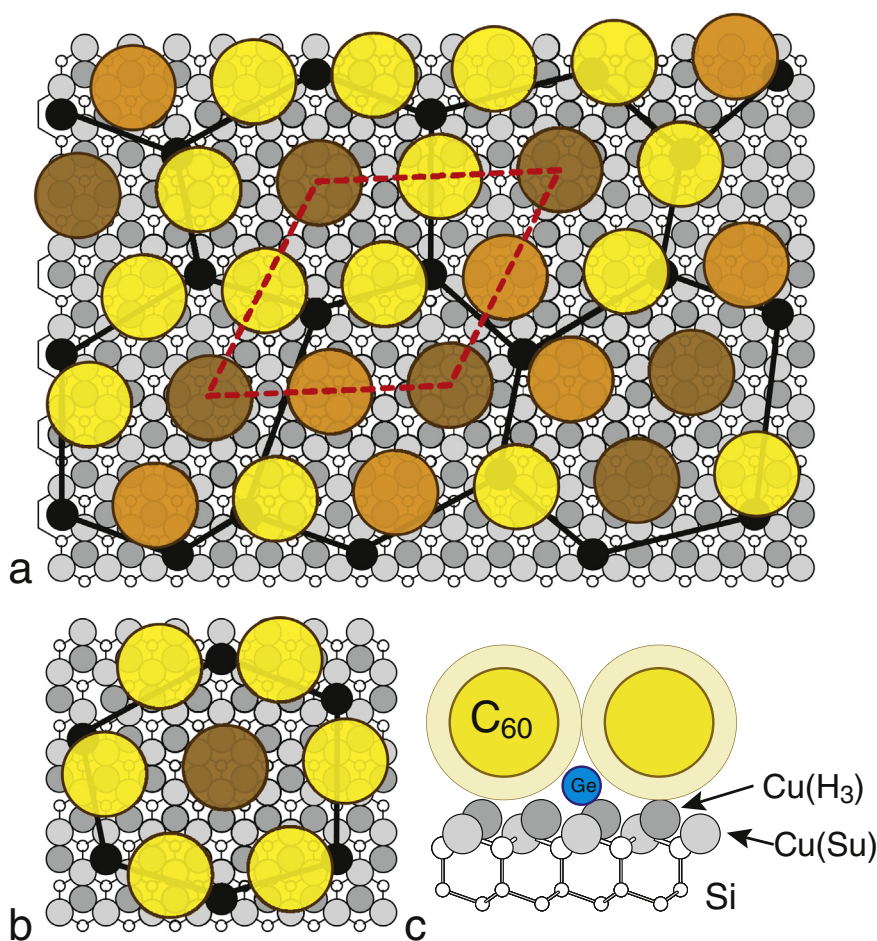


Fig. 5. (a) Schematic model illustrating the brightness of fullerenes as a function of their locations. Fullerenes residing close to the hexagon centers are shown by dark brown circles, those residing close to the domain boundaries and at the domain boundaries by orange and yellow circles, respectively. Copper atoms are shown by gray circles (with dark and light gray colors for Cu atoms occupying H_3 and S_u sites, respectively), Si atoms by small white circles. The 2×2 unit cell is outlined by dashed red frame. (b) Schematic illustration of how the seven-molecule cluster fits an almost regular hexagonal domain of the Si(111)'pseudo- 5×5 -Cu surface reconstruction. (c) Side view of the model structure of C_{60} fullerenes on the Ge-adsorbed Si(111)'pseudo- 5×5 -Cu surface where Ge atoms are shown by blue circles. The sizes of C_{60} molecules, Cu and Ge atoms are presented in the same scale. The inner (dense yellow) shells for C_{60} fullerenes correspond to their size, ~ 7 Å, the outer (light yellow) shell to their inter-molecular distance, ~ 10 Å. The sizes of circles for atoms correspond to their covalent radii. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

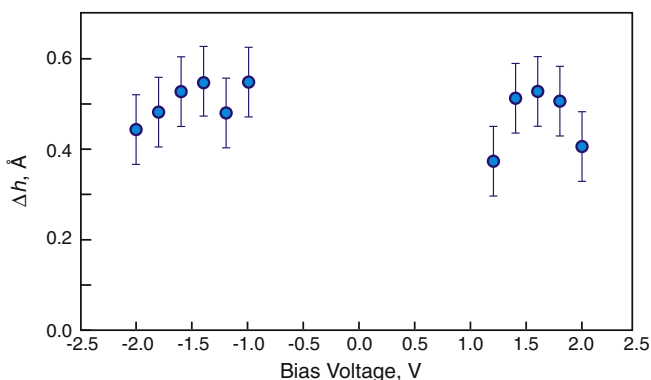


Fig. 6. Apparent height difference between bright and dim fullerenes in the STM images as a function of bias voltage.

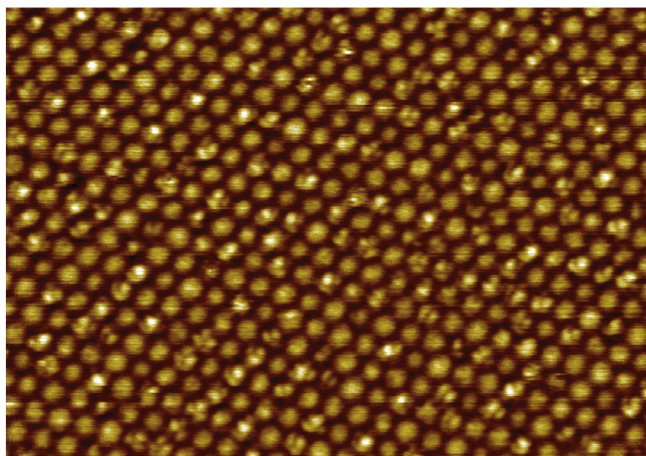


Fig. 7. High-resolution STM image of the C_{60} monolayer on the Ge-adsorbed $Si(111)$ pseudo- 5×5 -Cu surface. Occurrence of the intramolecular resolution for some fullerenes is an indication that they are fixed in a certain orientation and do not rotate.

opposite pattern, taking into account that Ge atomic clusters reside in the central regions of hexagons, hence C_{60} in the centers of hexagons are expected to sit atop Ge clusters and be higher than C_{60} molecules at the hexagon periphery where Ge atoms are absent. A possible explanation is that C_{60} fullerenes upon adsorption displace Ge atoms from their original sites and eventually they occupy interstitial sites in between C_{60} and produce small effects on C_{60} adsorption geometries. The suggestion seems to be quite reasonable since, first, Ge atoms in atomic cluster are actually not bonded directly to each other due to relatively large distances between them, $\sqrt{3}a_0$ or $2a_0$, and, second, there is a plenty of space for Ge atoms in between C_{60} taking into account the size of these atoms and molecules (see Fig. 5b).

Though at a glance, Ge atoms do not affect C_{60} adsorption geometry, a closer look revealed the sign of interaction between C_{60} and Ge. Namely, while at the pristine $Si(111)$ pseudo- 5×5 -Cu surface all fullerenes show up in STM images as featureless round protrusions, at the Ge-adsorbed $Si(111)$ pseudo- 5×5 -Cu surface some fullerenes display intramolecular features (Fig. 7). One can conclude that in the former case the fullerenes are in continuous rotation, while in the latter case some fullerenes are fixed in one of several types of orientation. For example, “three-lobe” appearance is known to correspond to C_{60} with hexagon on top, while “two-lobe” one to C_{60} with edge between two hexagons on top. Thus, Ge atoms hamper rotation of selected fullerenes at the $Si(111)$ pseudo- 5×5 -Cu surface.

4. Conclusion

In conclusion, formation of C_{60} molecular layers on the pristine and Ge-modified $Si(111)$ pseudo- 5×5 -Cu surfaces was studied using STM observations. Despite an apparent difference in the structural properties of the two surfaces, the C_{60} layer growth there is very similar. At the early growth stages, surface potential relief does not affect migration of adsorbed C_{60} molecules which are eventually accumulated along the step edges. At the stage of extended C_{60} array formation, the template effect of the underlying incommensurate surface reconstruction comes out in modulation of the C_{60} monomolecular layer which displays a quasi-periodic pattern of dim and bright fullerenes. The pattern has in average the 2×2 periodicity dictated by approximate coincidence of the doubled C_{60} - C_{60} intermolecular distance and $5.5a_0$ periodicity of the underlying substrate. In the case of the Ge-modified $Si(111)$ pseudo- 5×5 -Cu surface, fullerenes plausibly displace Ge atoms from their original positions to the interstitial sites in C_{60} layer where Ge atoms terminate rotation of selected fullerenes.

Acknowledgments

The work was supported by Russian Science Foundation under grant no. 14-12-00482.

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