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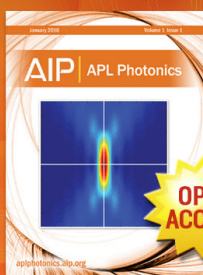J. Appl. Phys. **98**, 103528 (2005); 10.1063/1.2136423

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Incommensurate superstructure in heavily doped fullerene layer on Bi/Si(111) surface

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Cs adsorption onto the C_{60}-covered Si(111)-β-$\sqrt{3} \times \sqrt{3}$-Bi reconstruction has been studied by means of scanning tunneling microscopy and photoelectron spectroscopy. Unexpected increase in apparent size of every second C_{60} molecule has been detected, hereupon the close packed molecular array almost doubles its periodicity. The change affects only the fullerenes that are in direct contact with the metal-induced reconstruction and takes no place already in the second layer. Photoelectron studies have revealed that this incommensurate "2×2" superstructure of a heavily doped C_{60} monolayer remains in an insulating state regardless of doping level. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4928866]

I. INTRODUCTION

Alkali metal (AM) doped C_{60} compounds (fullerides) are fascinating objects for physics of strongly correlated systems owing to their properties, like superconductivity and metal-insulator transition.[1] Studies of AM-doped C_{60} monolayers on metal surfaces[2–7] gained a new insight into an interplay between Jahn-Teller (JT) distortion (charge-induced deformation of molecular cage[8]) and Mott-Hubbard (M-H) transition,[5] revealed novel orientational ordering,[6] etc.

Due to different interactions between molecules and substrate, fullerenes on semiconductors often behave differently than on metal surfaces.[9] AM doping of a C_{60} layer residing on a metal-induced reconstruction of silicon might involve complex three-party interactions leading to unexpected results. For example, it is understood that AM adsorption onto Si(111)-β-$\sqrt{3} \times \sqrt{3}$-Bi reconstruction results in incorporation of alkali atoms into the metal layer leading to significant charges in atomic arrangement and electronic structure of the surface.[10,11] In the present paper we report on Cs deposition onto the C_{60} layer grown on Si(111)-β-$\sqrt{3} \times \sqrt{3}$-Bi surface (β-$\sqrt{3}$-Bi hereafter) studied by means of scanning tunneling microscopy/spectroscopy (STM/STS) and photoelectron spectroscopy (PES) methods. We have observed the unusual ordering in the layer, as though every second molecule becomes isolated from the rest of the layer.

II. EXPERIMENTAL DETAILS

STM/STS and PES experiments were carried out in the same ultra-high 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.

Pristine β-$\sqrt{3}$-Bi reconstruction was formed by depositing 1 Ml Bi from Al_2O_3 crucible onto Si(111) surface held at ~400 °C. (1 Ml (monolayer) = 7.8×10^{14} cm^{-2}.) C_{60} was deposited from resistively heated Ta boat onto a room-temperature (RT) substrate at a rate of about 0.2 Ml/min (calibrated by direct counting the number of molecules in STM images). Cs deposition was performed using SAES dispenser. For calibration of Cs deposition rate, Cs-modified Si(111)-α-$\sqrt{3} \times \sqrt{3}$-Au reconstruction adopting about 0.1 Ml Cs[12] was used as a reference. Although its formation procedure requires annealing, the lowest possible temperature (~150 °C) was employed to prevent the loss of Cs atoms. We estimate the accuracy of Cs deposition at 20%.

STM images were acquired using Omicron variable-temperature STM VT-XA operating in a constant-current mode. For STM/STS experiments, mechanically cut PtIr tips cleaned by *in situ* heating were used. For STS measurements, dI/dV spectra were obtained by modulating V by 20 mV, 6 kHz AC signal.[13] STM/STS measurements were performed at 300 K.

PES measurements were conducted at 78 K using VG Scienta R3000 electron analyzer and high-flux He discharge lamp ($h\nu$ = 21.2 eV) with toroidal-grating monochromator as a light source.

III. RESULTS

The β-$\sqrt{3}$-Bi reconstruction was used as a substrate for fullerene layers growth. It consists of T_4-centered Bi trimers (milkstool model[14]) as shown in the inset of Fig. 1. On this surface C_{60} molecules form close-packed hexagonal arrays in the layer-by-layer mode (Fig. 1) that is typical for most of the metal-covered surfaces. In the present case the maximum reachable area of the first layer, which was of the primary
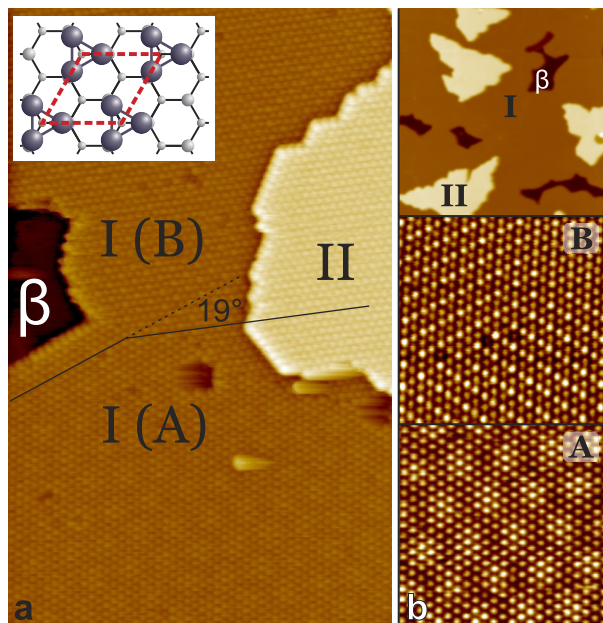

FIG. 1. (a) 75×47 nm^2 filled state (-2.0 V) STM image of C$_{60}$/$\sqrt{3}$-Bi surface prior to Cs deposition. "I," "II," and "β" labels stand for arrays of first and second layers and remain of the uncovered surface, respectively. Black lines demonstrate the difference in orientations between A and B arrays. Inset shows the structural model of the β-$\sqrt{3}$-Bi reconstruction where Bi and Si atoms are shown by violet and gray circles, respectively. (b) Large-scale 500×500 nm^2 image and 20×20 nm^2 images with enhanced contrast to emphasize corresponding moiré patterns.

interest, constitutes about 80% then the propagating second layer takes over the surface.

In STM images one can notice that the first layer demonstrates slight modulations of contrast (moiré patterns) originated from the mismatch between molecular layer and underlying $\sqrt{3} \times \sqrt{3}$ surface. In agreement with previous studies, the "A" array that is aligned along main crystallographic directions of Si(111) substrate demonstrates $\sqrt{19} \times \sqrt{19}$ moiré pattern.[15] The 19°-rotated "B" array generally shows no regular pattern, though some slight contrast difference that produces distorted 2×2 and 2×1 patterns can be detected. All fullerenes appear in STM images as featureless round protrusions. Lack of the intramolecular resolution is attributed to continuous rotation and is an indication of a weak interaction between surface and molecular layer.

The second layer does not inherit the moiré pattern and is almost completely featureless.

Upon Cs adsorption, the C$_{60}$/$\sqrt{3}$-Bi surface undergoes changes different from previously reported cases of AM/C$_{60}$ monolayers on metals.[5] The most prominent feature of STM images after Cs doping is the appearance of huge bright protrusions in the first layer, where both A and B arrays are equally involved (Fig. 2). At first glance the molecules grow in size twice, doubling the spacing between them. Apparent height difference is about 0.4 nm. Second layer patches (II) stay almost unaltered.

The modified array will further be noted as a "2×2" superstructure. The "normal" and modified lattices do not exactly match and positions of giant protrusions are not precisely "every-second" as imagined at a glance, indicating some lateral rearrangements in the modified array rendering the
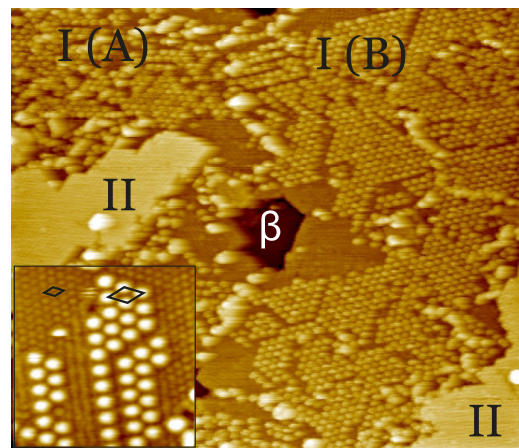

FIG. 2. 120×100 nm^2 filled state (-1.4 V) STM image recorded after ~1 Ml of Cs adsorption at RT. Inset shows the 20×20 nm^2 image where small and big rhombuses mark unit cells with $a = 1.04$ nm and $a = 1.98$ nm, respectively.

"2×2" superstructure incommensurate. Arranging of fullerenes into a superstructure is not a surprise,[16,17] but usually it manifests itself as a lateral height variation, alternating bright and dim molecular contrast. Increase in apparent size of every second C$_{60}$ hiding the rest of them is rather unexpected. Note that both the apparent height (brightness) and the diameter of protrusions are increased roughly by the same value. It might indicate that the vertical displacement is negligible, otherwise the increase in the apparent height must prevail. Although we cannot completely rule out the extrusion of molecules up out of the layer, this alone cannot produce the aforementioned changes.

In the course of Cs deposition, we did not observe a serial formation of Cs$_x$C$_{60}$ compounds with different composition; the structure shown in Fig. 2 develops almost from the beginning of deposition and area, occupied by the enlarged protrusions, is proportional to the Cs coverage. Although the final Cs coverage roughly corresponds to 6-7 Cs atoms per each fullerene, pronounced disorder, obvious difference between first and second layers, possible Cs accumulation on the remains of β-$\sqrt{3}$-Bi reconstruction and between layers prevents us to establish conclusively an actual composition of the obtained Cs$_x$C$_{60}$ surface.

Further Cs adsorption leads to deterioration of the surface ordering (degradation of both layers, appearance of random islands, etc.).

There are another STM features that always accompany modified fullerenes, namely, continuous lines as though molecules were merged together (open arrows in Fig. 3). These polymer-like features are either straight or, in the immediate vicinity to a "2×2" array, adopt its periodicity. The chains consist of equally spaced (~0.5 nm) oval protrusions.

Changes in the surface electronic structure are consistent in general with those reported for AM-doped C$_{60}$ solids[18] and monolayers located on metal substrates.[2] PES spectra of the initial C$_{60}$-covered surface (Fig. 4(a)) show the HOMO (at about -2.3 eV) and HOMO+1 peaks (at about -3.7 eV). Unlike vast majority of reported cases of C$_{60}$ monolayers on metal surfaces,[19–23] no LUMO-derived bands in the vicinity of E_F were detected, indicating the absence of charge transfer from
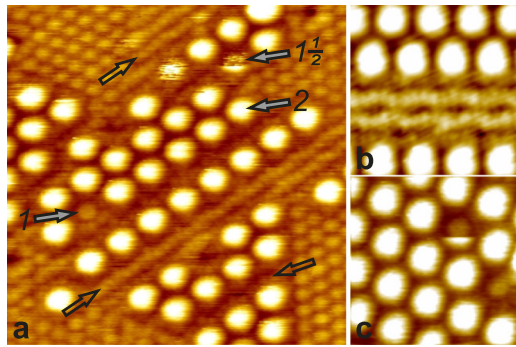
FIG. 3. (a) High-resolution 20×20 nm^2 filled state (-1.4 V) STM image of the surface after Cs adsorption. See text for the explanation about arrows. Close-ups of (b) polymer-like chains and (c) sudden change of protrusion *2* to *1* (also marked as "$1\frac{1}{2}$" in (a)).

the substrate to molecules. (Small peak at -1.6 eV corresponds to the top of the Si valence band.) Cs adsorption results in rising of a new peak in the HOMO-LUMO gap at -0.35 eV. With higher Cs coverage the peak slightly changes its position to -0.52 eV and a small shoulder appears at higher energy that might be a phonon satellite.[2,24] Angle-resolved PES (not shown here) revealed that this peak has no recognizable $E(\mathbf{k})$ dispersion.

A_xC_{60} materials are either metal with non-zero DOS at E_F ($x = 3$) or Mott-Hubbard insulator ($x = 4$).[18] At $x = 5$ monolayers return to metallic state.[6] In the present case, PES spectra clearly show the vanishing photoelectron intensity
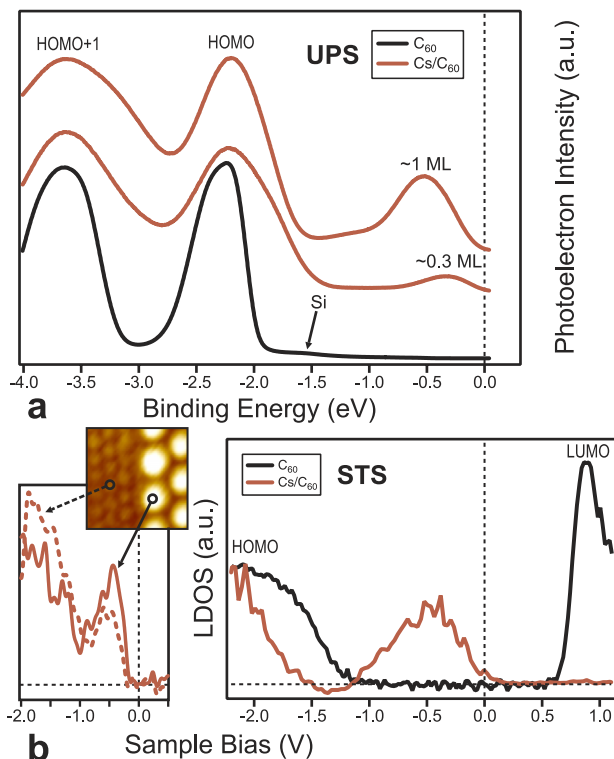

FIG. 4. Electronic structure of the Cs/C$_{60}$/β-$\sqrt{3}$-Bi system. (a) Angle-integrated He-Iα PES spectra obtained for C$_{60}$ monolayer prior (black line) and after (red lines) Cs adsorption at RT. Spectra for two Cs coverages are shown. (b) STS spectra for the same surfaces. Spectra in the right panel are averaged over 3×3 nm^2 area, in the left panel obtained in indicated points for the Cs-doped surface.

at E_F with no noticeable Fermi cutoff from the beginning of Cs adsorption, suggesting the insulating properties of the Cs/C$_{60}$/$\sqrt{3}$-Bi system.

STS measurements (Fig. 4(b)) are in agreement with PES data. Initial position of LUMO level (at about $+1$ eV) indicates the reduced coupling with the surface.[22,25,26] Note that both "2×2" protrusions and surrounding array display similar electronic structure (Fig. 4(b), left panel) despite the striking difference in STM appearances. It may indicate the rather uniform distribution of Cs atoms among the first C$_{60}$ layer.

IV. DISCUSSION

Since no significant variations in the areas, occupied by both layers and voids were detected during Cs deposition, one can admit only a slight redistribution of molecules. Judging from the STM appearance ("two-lobe"), polymer-like chains (open arrows in Figs. 3(a) and 3(b)) must be either rows of C$_{60}$ with enhanced fixation to the surface having hexagon-hexagon (*h-h*) bond up orientation[27] or that of C$_{60}^{4-}$ molecules influenced by severe JT distortion.[5,6] High value of AM-doping, insulating properties, and perfectly correlated orientations inside the row are arguments in favor of the latter.

Consider protrusion *1* in Fig. 3 that shows up as a normal-size fullerene. It is located inside the "2×2" array instead of one of a giant protrusion *2*. We have observed how *2* switched to *1* occasionally and vice versa. For example, $1\frac{1}{2}$ in Figs. 3(a) and 3(c) indicate the *2* protrusion in the halfway changing to *1*. (STM images are acquired from bottom to top.) Since it displays no intermolecular structure, it is possible in continuous rotation like the rest of normal-size fullerenes.

Origin of the $1 \rightarrow 2$ transition that doubles the apparent size of a fullerene can hardly be explained by any reasonable structural transformations. Instead, it can be understood as follows. In general, a finite tip apex increases size of a STM protrusion,[28] so an isolated C$_{60}$ usually appears broader than that inside of a close-packed array. For instance, Fig. 5 shows C$_{60}$ adsorbed on Si(111)7×7 at RT. In agreement with early studies,[9] instead of forming a close packed islands, fullerenes prefer to scatter as isolated molecules (*2* in Fig. 5(a)) having apparent diameter of $\sim$2 nm. (It always exceeds the real size of molecular cage in free space.[29]) However, if their amount is sufficient, in some regions a rudimentary packing can be seen (*1* in Fig. 5(a)); STM features overlap leaving protrusions with
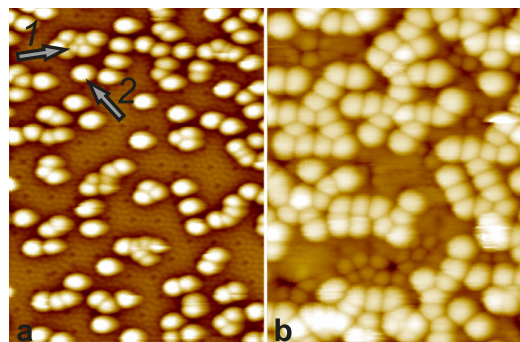

FIG. 5. 30×40 nm^2 STM images of (a) C$_{60}$ adsorbed on Si(111)7×7 surface and (b) Cs-modified C$_{60}$ monolayer on the Bi(0001)/Si(111) thin film.

diameters of about 1 nm. Thus, we argue that the *1 → 2* transition can be accounted for a sudden self-isolation of an every second molecule from neighbors, although it is still located inside a close packed array. The $C_{60}/7 \times 7$ gained its high contrast by receiving charge from the surface while the initial C_{60}/β-$\sqrt{3}$-Bi is not charged (recall the absence of a LUMO-derived band). Cs atoms donate electrons to C_{60} transferring some of them into a state similar to an isolated molecule on 7×7. This behavior must be originated from a strong electron repulsion between highly charged particles. However, formation of a superstructure goes beyond a simple model of Mott insulator, where electrons localize on each site of a crystalline lattice. Besides, in contrast to most $AM/C_{60}/$metal systems, the initial β-$\sqrt{3}$-Bi reconstruction actively interacts with AM leading to significant atomic rearrangement in the Bi layer.[10,11] Complete understanding of processes in such complex system requires intensive density functional theory (DFT) calculations that is beyond the scope of the present paper.

We performed the same experiment changing the β-$\sqrt{3}$-Bi reconstruction to Bi(001) thin film that can be grown on the Si(111) surface.[30] A similar phenomenon has been observed except for formation of a regular superlattice (Fig. 5(b)). Lack of the long-range order emphasizes the similarity to an array of isolated charged fullerenes (the $C_{60}/7 \times 7$ case) even more when oversized protrusions overlap rendering triangular or rectangular apparent shapes of fullerens. (Note that again only the half of molecules can be seen in the former close-packed array.)

V. CONCLUSION

Upon Cs doping, C_{60} monolayer on a bismuth-covered Si(111) surface remains in an insulating state regardless of doping level in contrary to AM-doped fullerene layers on metal surfaces. Accepting charge from Cs atoms, every second molecule displays an unusual for close packed layers high STM contrast, consistent with isolated molecule. In the C_{60}/β-$\sqrt{3}$-Bi system, fullerenes with increased apparent size form the incommensurate "2×2" superstructure that is accompanied with the formation of polymer-like chains. In contrast, same Cs-doped monolayer on Bi(001) film shows the complete lack of ordering. Both surfaces are vivid examples of low-dimensional strongly correlated molecular system.

ACKNOWLEDGMENTS

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