



Adsorption and self-assembly of fullerenes on $\text{Si}(111)\sqrt{3} \times \sqrt{3}\text{-Ag}$: C_{60} versus C_{70}



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ABSTRACT

Behavior of C_{60} and C_{70} fullerenes adsorbed onto $\text{Si}(111)\sqrt{3} \times \sqrt{3}\text{-Ag}$ is compared on the basis of STM observations. Such characteristics as sticking coefficient, migration rate, attachment/detachment rate from the molecular islands are considered. Room-temperature sticking coefficient for C_{70} is slightly greater than that for C_{60} . Due to their non-spherical shape, C_{70} are less mobile than spherical C_{60} . For both types of fullerenes, mobility of molecules on the fullerene layer is significantly retarded as compared to that on bare $\text{Si}(111)\sqrt{3} \times \sqrt{3}\text{-Ag}$ surface. Self-assembly of C_{60} obeys layer-by-layer growth mode, while C_{70} follows multi-layer mode, a sign of a greater Ehrlich-Schwoebel barrier. Alternating deposition of C_{60} and C_{70} paves the way to fabricate planar $\text{C}_{60}/\text{C}_{70}$ heterostructures with the most promising results being obtained with nanostructured islands grown on C_{60} monomolecular layer.

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1. Introduction

Fullerene adsorption and self-assembly on the various metal and semiconductor surfaces attract considerable interest, in particular, due to potentially valuable applications of fullerene layers in nanoscale devices. Metal-induced reconstructions on semiconductor (e.g., Si) surfaces show up as a specific class of template surfaces, that differ essentially in structure and properties from both pure metal and semiconductor surfaces. If one addresses C_{60} interaction with various metal-reconstructed Si surfaces, the $\text{Si}(111)\sqrt{3} \times \sqrt{3}\text{-Ag}$ surface opens the list of the most extensively studied templates [1–9]. The high-quality homogeneous $\text{Si}(111)\sqrt{3} \times \sqrt{3}\text{-Ag}$ surface with a negligible density of point defects can be easily prepared just by saturating adsorption of Ag on the $\text{Si}(111)7 \times 7$ surface held at about 500 °C. Atomic arrangement of the $\text{Si}(111)\sqrt{3} \times \sqrt{3}\text{-Ag}$ surface is well-established to be described by the inequivalent triangle (IET) model [10, 11]. Thus, bearing in mind the available background, easy preparation of high-quality surface and well-established atomic structure, the $\text{Si}(111)\sqrt{3} \times \sqrt{3}\text{-Ag}$ reconstruction

is believed to be an appropriate playground for studying fine effects of fullerene adsorption, in particular the role of fullerene size and shape.

In the present paper, we report on the results of comparative study of C_{60} and C_{70} adsorption and self-assembly on $\text{Si}(111)\sqrt{3} \times \sqrt{3}\text{-Ag}$ surface. Using scanning tunneling microscopy (STM) observations at room temperature (RT) and 115 K, we have addressed such characteristics as sticking coefficient, migration rate, attachment/detachment rate from the molecular islands for C_{60} and C_{70} fullerenes. Estimations for some of these parameters have been acquired. In conclusion, we have considered possibility of growing planar $\text{C}_{60}/\text{C}_{70}$ heterostructures using alternating deposition of C_{60} and C_{70} and demonstrated that the most vivid results can be obtained with fullerene nanostructured islands grown on fullerene monomolecular layer.

2. Experiment

Our experiments were performed with an Omicron VT-STM operating in an ultrahigh vacuum ($\sim 2.0 \times 10^{-10}$ Torr). Atomically-clean $\text{Si}(111)7 \times 7$ surfaces were prepared in situ by flashing to 1280 °C after the samples were first outgassed at 600 °C for several hours. Silver was deposited from an Ag-wrapped tungsten filament. The

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high-quality $\text{Si}(111)\sqrt{3} \times \sqrt{3}$ -Ag surface with a negligible density of point defects was prepared by saturating adsorption of about 1 ML Ag onto the $\text{Si}(111)7 \times 7$ surface held at 500 °C. Fullerenes, C_{60} (Alfa Aesar, purity 99.92%) and C_{70} (BuckyUSA, purity 99.5%), were deposited from resistively heated Ta boats. For STM observations, electrochemically etched tungsten tips cleaned by *in situ* heating were employed.

3. Results and discussion

In agreement with the previous STM studies, we have found that upon RT adsorption onto $\text{Si}(111)\sqrt{3} \times \sqrt{3}$ -Ag surface C_{60} fullerenes self-assemble into the close-packed hexagonal arrays in two azimuthal orientations, i.e. with C_{60} molecular rows making an angle of either 19.1° (19.1°-rotated arrays) or 30° (30°-rotated arrays) with the main crystallographic direction of $\text{Si}(111)$, $[\bar{1}10]$. The 19.1°-rotated arrays definitely prevail over 30°-rotated arrays (Fig. 1a). Other orientations of the C_{60} arrays can also occur occasionally. For example, presence of the $\text{Si}(111)6 \times 1$ -Ag domains on the surface can trigger the growth of 0°-rotated arrays (i.e., those where C_{60} rows are aligned along the $[\bar{1}10]$ direction). In order to avoid this effect, we have ensured that the $\sqrt{3} \times \sqrt{3}$ -Ag reconstruction occupies the entire surface in all experiments. Like C_{60} molecules, C_{70} fullerenes also self-assemble into the close packed hexagonal arrays, but with the different orientations. For C_{70} , the 0°-rotation is the major orientation followed by the 30°-rotation (Fig. 1b).

Peculiar feature of the C_{60} monolayers is a presence of the dark features within fullerene arrays [3, 8]. They were first interpreted as missing-molecule defects [3], but have recently been recognized as “dim C_{60} ” fullerenes residing ~ 1.6 Å lower than the other (“normal”) C_{60} fullerenes due to disintegration of Ag trimers on $\text{Si}(111)\sqrt{3} \times \sqrt{3}$ -Ag under given fullerenes [8]. While the normal C_{60} are in continuous rotation, the dim C_{60} are fixed in one of the single orientations, indicating a tight binding to the surface [8]. C_{70} arrays also contain dim fullerenes which have the same origin, namely they are located lower than other molecules and are fixed in certain orientations (Fig. 2a). As a result, they display characteristic intermolecular structures in the high-resolution filled-state STM images (Fig. 2b, c, d, e, f). It is worth noting that behavior of dim C_{70} fullerenes appears very similar to that of dim C_{60} [8]. An additional feature which is specific for C_{70} arrays is that the “normal” fullerenes display somewhat different STM contrast. This is clearly seen in Fig. 2a where neighboring C_{60} and C_{70} arrays are shown. The difference can reasonably be attributed to variety of adsorption geometries for the non-spherical C_{70} molecules (e.g., with “standing”, “lying” and “inclined” molecules). The vertically standing C_{70} fullerenes display the brightest STM contrast and they can be considered as super-bright C_{70} . The other specific feature is a presence of vacancies (i.e., real missing-molecule defects) within C_{70} arrays, but their occurrence is actually very seldom. They are shown in Fig. 2g and h, including the vacancy which became filled by C_{70} in the course of STM scanning (Fig. 2h).

When the deposited fullerene coverage is close to one monomolecular layer, essential difference in the fullerene layer morphology becomes apparent for C_{60} and C_{70} (Fig. 3). The C_{60} growth follows almost ideal layer-by-layer mode, namely, patches of the second molecular layer appear only when the first layer is close to completion (Fig. 3a). In contrast, the growth mode for C_{70} is almost multi-layer one, in which case growth of the second and even the third layers start well before completion of the first layer (Fig. 3b). The change of the growth mode from layer-by-layer to multi-layer one might be caused either by suppressed fullerene migration over the first molecular layer or by the presence of the noticeable Ehrlich-Schwoebel barrier that hampers crossing molecular step by the

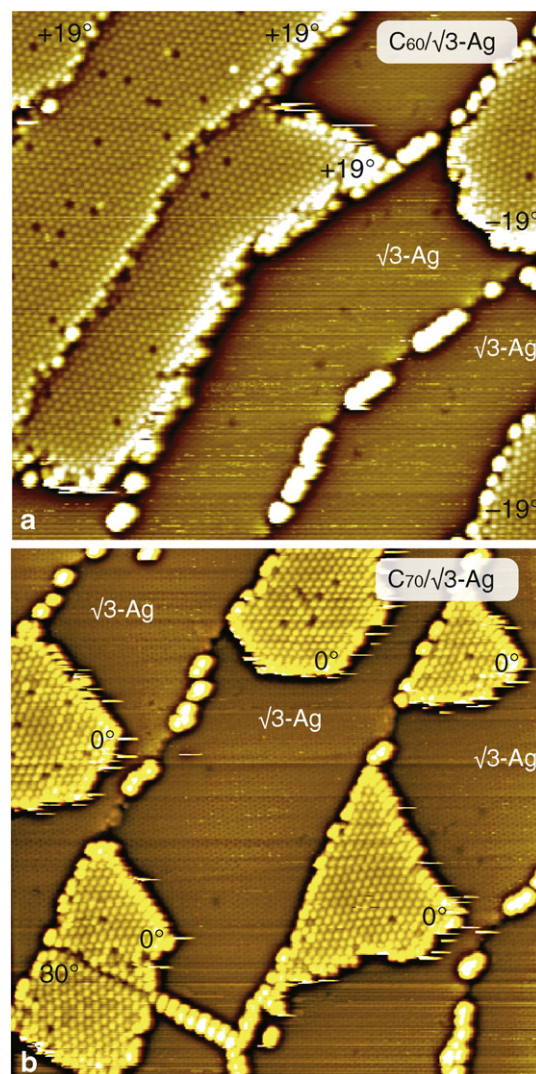


Fig. 1. $750 \times 750 \text{ \AA}^2$ STM images of (a) C_{60} and (b) C_{70} arrays grown on $\text{Si}(111)\sqrt{3} \times \sqrt{3}$ -Ag surface at RT. The orientations of the arrays (i.e., angles which molecular rows make with the main crystallographic direction of $\text{Si}(111)$, $[\bar{1}10]$) are indicated.

fullerenes (i.e., fullerene jumping down to the $\sqrt{3} \times \sqrt{3}$ -Ag surface). To elucidate, at least semi-quantitatively, these characteristics as well as some others, we have explored fullerene behavior not only at RT, but also at low temperature of ~ 115 K.

In particular, it was noticed that after similar doses, fullerene coverages at RT were systematically lower than those at 115 K, that means that fullerene sticking probability s is not equal 1.0 at RT. Assuming $s = 1.0$ for adsorption at 110 K, it was found that s is about 0.6–0.7 for RT C_{60} adsorption onto $\text{Si}(111)\sqrt{3} \times \sqrt{3}$ -Ag and ~ 0.8 for C_{70} under the same conditions. Remarkably, heating of the molecular layers formed at 115 K to RT does not change the fullerene coverage. Thus, one can conclude that there are plausibly two adsorption states of fullerene at $\text{Si}(111)\sqrt{3} \times \sqrt{3}$ -Ag. The first one is the precursor state when fullerene migrates over the terrace and might desorb from the surface. The second one is the stable state when fullerene becomes attached to atomic step or fullerene array.

Let us characterize now surface migration of fullerenes in the framework of the rate equation theory which establishes a quantitative relation between island density N as a function of deposition rate R and growth temperature T and characteristics of the processes

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