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C_{70} self-assembly on In- and Tl-adsorbed Si(111)$\sqrt{3} \times \sqrt{3}$-Au surfaces

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ABSTRACT

Behavior of C_{70} fullerenes adsorbed onto the In- and Tl-modified Si(111)$\sqrt{3} \times \sqrt{3}$-Au surfaces at room temperature (RT) and 112 K has been studied using scanning tunneling microscopy observations and compared with the known results for the C_{60}s on the same surfaces. During island growth at 112 K, both C_{70} and C_{60} are characterized by the same critical island size i=1. The difference is in an island shape as C_{70}s tend to form chain-like islands built of double or triple molecular rows along the [$\bar{1}$10] Si(111) substrate directions. At RT, C_{70}s have a lower mobility as compared to C_{60}s. In contrast to the C_{60} magic islands, the C_{70} islands do not demonstrate any strong preference for specific shapes or sizes. Extended C_{70} arrays exhibit a stripe-like 3×1 reconstruction where a single row of bright fullerenes mediated by a double row of dim fullerenes. The reconstruction is due to the different orientations of C_{70}s within the layer which does not relate to the structure of the underlying Au/Si(111) substrate. This is in contrast to the hexagonal reconstructions of C_{60}s where the bright fullerenes occupy the specific adsorption site atop Au trimers. The difference in the behavior of C_{70} and C_{60} is plausibly affected by the non-spherical shape of C_{70} molecule and a greater intermolecular C_{70}-C_{70} interaction.

1. Introduction

The adsorption of fullerenes onto metal and semiconductor surfaces has attracted considerable interest due to a variety of the fascinating phenomena underlying fullerene self-assembly. Among such phenomena one can mention developing modulations in the close-packed fullerene monolayers which shows up as appearance of molecules having two different contrast in scanning tunneling microscopy (STM) images: “bright” and “dim”. The bright-dim contrast was observed in C_{60} monolayers on many noble-metal surfaces, including Ag(111) [1,2], Ag(100) [3–5], Au(111) [6–9], Cu(111) [10], Cu(100) [11]. The apparent height difference between bright and dim molecules can amount to ~1–2 Å. However, the origin of this contrast remains a debated subject as it can result from the electronic effects, the molecular orientations, or the geometric effects due to substrate reconstruction. As for the metal/silicon surface phases, i.e. surface reconstructions induced by adsorption of metal submonolayers onto Si crystalline substrates, the distinct dim-bright contrast was observed in the C_{60} monolayers on the pristine Si(111)$\sqrt{3} \times \sqrt{3}$-Ag surface [12,13] and Si(111)$\sqrt{3} \times \sqrt{3}$-Au surface modified by In [14,15] or Tl [16] adsorption. In particular, the dim fullerenes in the C_{60} monolayers on Si(111)$\sqrt{3} \times \sqrt{3}$-Ag constitute ~10% of all fullerenes and reside ~1.6 Å lower than other fullerenes. It was suggested that formation of the dim C_{60} is associated with a disintegration of Ag trimer of Si(111)$\sqrt{3} \times \sqrt{3}$-Ag surface beneath a given fullerene [13]. In the C_{60} monolayers on the In- or Tl-adsorbed Si(111)$\sqrt{3} \times \sqrt{3}$-Au surfaces, the bright fullerenes are arranged in the well-defined two-dimensional (2D) lattices [14,16]. Note that adsorption of ~0.1–0.2 ML of In or Tl onto Si(111)$\sqrt{3} \times \sqrt{3}$-Au was used to remove domain walls, characteristic of the pristine surface [17], and to produce almost defect-free highly-ordered and homogeneous Si(111)$\sqrt{3} \times \sqrt{3}$-Au surfaces [18–20]. These surfaces preserve atomic arrangement of the pristine surface [21] but contains also a 2D gas of In or Tl adatoms. The bright C_{60} on these surfaces were recognized to reside directly atop the Au trimers, the most energetically unfavorable adsorption sites [14,15]. This fact has a remarkable sequence for the C_{60} island growth leading to size selection and magic C_{60} island formation. For example, more than 80 % of C_{60} islands grown on In-adsorbed Si(111)$\sqrt{3} \times \sqrt{3}$-Au surface can have identical shape and size, namely each contains 37 fullerenes arranged in a regular hexagon [15]. Bearing in mind this advantageous property of the particular fullerene-substrate pair, it seemed of interest to explore how changing of the spherical fullerenes C_{60} for the elongated fullerenes C_{70} would affect their growth mode. It is worth noting, however, that in many adsorption phenomena, C_{70} differ from C_{60} not only by the size and shape but rather by the different charge transfer [22], kinetic characteristics [23] and intermolecular interaction [24].

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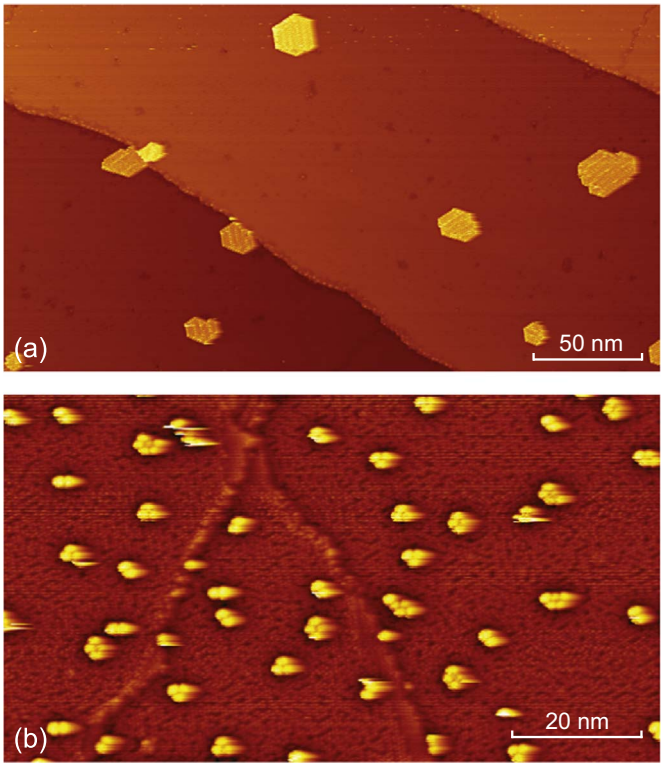

Fig. 1. STM images illustrating early stage of C_{70} island growth on In-adsorbed Si(111)$\sqrt{3} \times \sqrt{3}$-Au held at (a) RT and (b) 112 K. Scale: (a) 300 × 165 nm^2, (b) 100 × 55 nm^2.

In the present paper, we report on the results of the STM study of C_{70} adsorption and self-assembly on In- and Tl-adsorbed Si(111)$\sqrt{3} \times \sqrt{3}$-Au surface which results are compared with those reported for C_{60} on the same surfaces. It has been found that non-spherical shape of C_{70} alters significantly the growth mode. Starting from the early stages, the islands tend to adopt elongated shapes. In the extended arrays, the molecules are arranged in the linear superstructure with alternating sequence of bright and dim C_{70} rows, namely one bright row is typically mediated by two dim rows. The superstructure does not demonstrate a clear resemblance with the structure

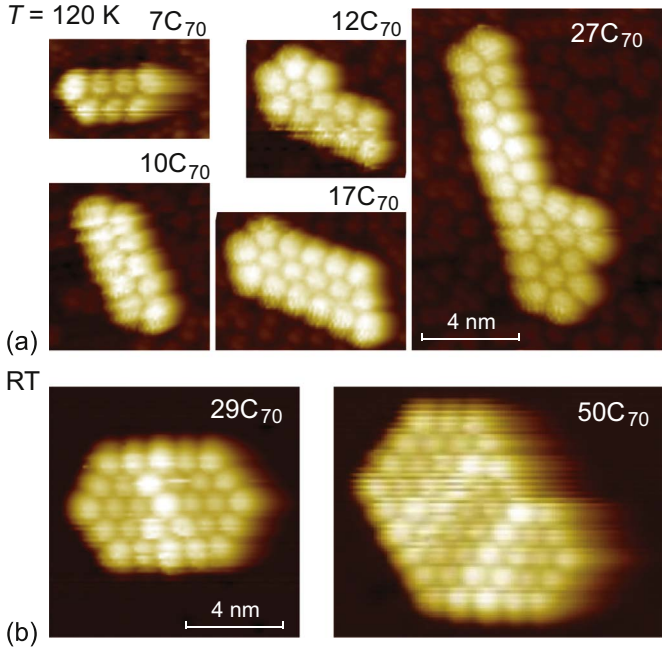

Fig. 3. Selection of C_{70} islands grown at (a) 112 K and (b) RT.

of the underlying Au/Si(111) substrate and is plausibly a result of the interactions between molecule in various orientations.

2. Experiment

Our experiments were performed with an Omicron VT-STM operating in an ultrahigh vacuum (~2.0 × 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. Gold was deposited from an Au-wrapped tungsten filament, indium and thallium from the Ta crucibles and fullerenes, C_{70} (BuckyUSA, purity 99.5%), from a resistively heated Ta boat. For STM observations, electrochemically etched tungsten tips cleaned by *in situ* heating were employed. To prepare the In- or Tl-modified Si(111)$\sqrt{3} \times \sqrt{3}$-Au surfaces, the Si(111)$\sqrt{3} \times \sqrt{3}$-Au surface was first formed by Au deposition onto Si(111)7 × 7 surface held at 600° C and then ~0.5 ML of In or Tl was

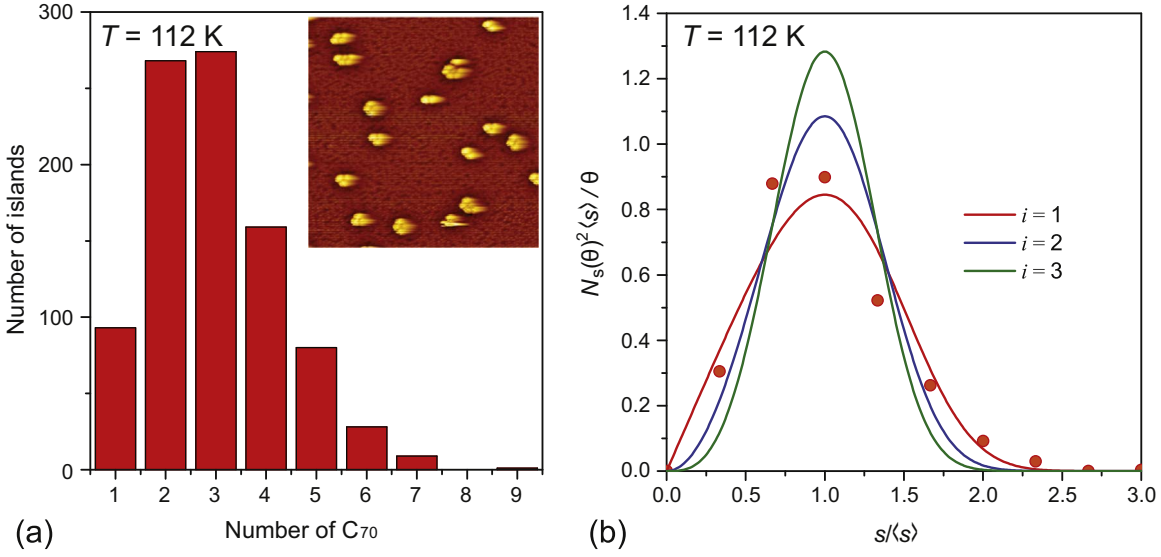

Fig. 2. (a) Experimental C_{70} island size distribution at 112 K. Inset shows a fragment of the surface with C_{70} island array under consideration. (b) Experimental scaled island size distribution (red circles) superposed on the simulated scaling functions f_i for critical island size i=1, 2, and 3 (red, blue and green lines, respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)