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Peculiar diffusion of C_{60} on In-adsorbed Si(111)$\sqrt{3} \times \sqrt{3}$-Au surface

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ABSTRACT

In-accumulated Si(111)$\sqrt{3} \times \sqrt{3}$-Au surface represents a highly-ordered homogeneous Au/Si(111) reconstruction with a two-dimensional gas of In adatoms on it. Regularities of C_{60} migration on this surface have been elucidated through analysis of C_{60} island density as a function of growth temperature and deposition rate in the framework of the rate equation theory and simulation of C_{60} migration using density-functional-theory calculations. The critical cluster size has been found to be $i = 1$ for the whole temperature range studied, from 110 to 240 K, while activation energy for C_{60} diffusion varies from (99 ± 18) meV at 110 ÷ 140 K to (370 ± 24) meV at 160 ÷ 240 K. This finding has been accounted to the peculiarity of C_{60} migration in a labyrinth built of In adatoms on the Si(111)$\sqrt{3} \times \sqrt{3}$-Au surface, namely, at low temperatures C_{60} migration is confined within the labyrinth channels, while at high temperatures C_{60} molecules possess enough thermal energy to surmount the labyrinth walls.

1. Introduction

Elucidating the regularities of atomic and molecular island formation has been a long-standing problem in surface physics and material science. Considerable efforts in this field have resulted in developing powerful theoretical approaches. In particular, the rate equation theory establishes a quantitative relationship between the island density N (which can be directly measured in the experiment as a function of deposition rate R and growth temperature T) and characteristics of the atomic processes involved in island formation, including a surface diffusion barrier of adatoms E_{diff}, a critical island size i and a binding energy E_i gained in forming the critical island [1]:

$$N \propto \left(\frac{R}{\nu_0}\right)^{i/(i+2)} \exp\left(\frac{iE_{\mathrm{diff}} + E_i}{(i+2)k_B T}\right) , \quad (1)$$

where ν_0 is the attempt frequency and k_B is the Boltzmann constant. Remind that a critical island size i is defined as one less than the number of atoms needed to form the smallest stable island. Efficiency of this classical approach (confirmed also with Monte Carlo simulations [2]) has been proved in the numerous studies on island formation in the variety of adsorbate–substrate systems [3–7]. Recently, the approach has been extended for more complicated cases (e.g., island growth mediated by formation of mobile clusters [8] or growth of compound islands [9,10]).

In recent years, self-assembly of the adsorbed molecular species into complex supramolecular structures has attracted considerable attention motivated by potential applications in molecular electronics. Fullerene C_{60} is believed to be a fascinating molecule from a nanoelectronics and nanoscience perspective. It is thought to be an ideal block for molecular devices due to its ability to accept electrons from other molecules, atoms, and surfaces [11]. Peculiarities of C_{60} island growth on the bare substrate surfaces [12–15] as well as those modified by adsorption of foreign atoms or molecules [16–21] have recently attracted a considerable interest. As for characterization of the C_{60} surface diffusion, monitoring of a single molecule migration [22,23] and evaluation of island density using the rate equation theory [14] have demonstrated their efficiency.

In this work, we employed the latter approach for characterization of C_{60} diffusion on Si(111)$\sqrt{3} \times \sqrt{3}$-Au surface. Before C_{60} deposition, the surface was modified by adsorption of ~0.14 ML of In to eliminate the domain wall network [24] characteristic of the original Au/Si(111) surface [25]. This surface has been shown to possess advanced properties of a perfect isotropic two-dimensional electron-gas system [26] with a large spin splitting of the surface state bands [27] which can be affected by adsorption of C_{60} molecules due to their acceptor-type behavior [28]. The properly prepared Si(111)$\sqrt{3} \times \sqrt{3}-(\mathrm{Au,In})$ surface is highly-ordered and contains extremely low density of surface defects. The presence of the 2D gas of In adatoms is its peculiar feature which

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allows to explore an interesting case of surface diffusion when two types of species, adatoms and molecules, are involved simultaneously in the diffusion process. We have found that while a critical island size $i = 1$ remains the same for the whole temperature range studied, the diffusion barrier for C_{60} is ~3.7 times greater for the "hot" surface (370 meV at 160–240 K) than for the "cold" surface (99 meV at 110–140 K). Possible origin of the phenomenon is discussed basing on the results of the density-functional-theory (DFT) calculations.

2. Experimental and calculation details

Our experiments were performed with an Omicron STM operating in an ultrahigh vacuum (~7.0×10^{-11} 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 from Ta crucible and C_{60} fullerenes from a resistively heated Mo crucible. For STM observations, electrochemically etched tungsten tips cleaned by in situ heating were employed.

To prepare the highly-ordered homogeneous In-adsorbed Si(111) $\sqrt{3} \times \sqrt{3}$-Au surface, the following procedure was used. First, the Si(111)-α-$\sqrt{3} \times \sqrt{3}$-Au surface [25] was formed by Au deposition at 700 °C. Then, ~0.5 ML of In was deposited onto this surface held at room temperature followed by brief (~15 s) annealing at 400 °C. The resultant surface preserves the atomic arrangement of pristine Si(111) $\sqrt{3} \times \sqrt{3}$-Au phase described by the conjugate-honeycomb chained trimer model [29–31,27]. It contains also ~0.14 ML of In left after high-temperature treatment and forming a 2D gas of adatoms [24,26].

To elucidate the experimental observations, systematic first-principle calculations based on the density functional theory (DFT) are performed. We employ the Vienna ab-initio simulation package (VASP) [32,33] with the projector augmented wave [34] pseudopotentials. In previous DFT calculations, the local density approximation [35,36] (LDA) has been shown to be able to well describe both the electronic and energetic properties of C_{60} adsorbed onto Au(111) [37,38] Ag(111) [38,39], and Ag(100) [37]. However, LDA describe the van der Waals (vdW) forces less accurately, which is important in C_{60}–metal and C_{60}–C_{60} interactions [40]. Therefore, in this work, the non-local van der Waals density functional (vdW-DF2) [41–43] method as implemented in VASP code has been employed. The Kohn–Sham wave functions are represented using a plane-wave basis set with a kinetic energy cutoff of 300 eV. The surface is simulated by a repeated slab with a $2\sqrt{3} \times 2\sqrt{3}$ lateral periodicity in which one Si + Au surface layer and four Si bi-layers are included. All atoms in the simulation model are fully relaxed except one bottom Si bi-layer is fixed at their bulk positions, and hydrogen atoms are used to passivate the Si dangling bonds at the bottom surface of the slab in the fixed positions. The vacuum region between slabs was ~17 Å. The Brillouin zone integration is performed with a $3 \times 3 \times 1$ k-point mesh which produces the well-converged results. The geometry is optimized until the total energy is converged to 10^{-4} eV. We applied the nudge elastic band (NEB) method [44] to find the energy barrier for the given diffusion pathways. NEB procedures interpolate a series of atomic configurations (so-called images) aligned in a pathway between the specific initial and final states, and then optimize these images by minimizing the total energies of the string images. In this way, the energy profile of diffusion process is obtained and the diffusion energy barrier is also revealed. In this study, we used a set of fifteen images including initial and final states to describe each diffusion pathway (except for the pathway A–B–C, where twenty-one images were used).

3. Results and discussion

Fig. 1 summarizes the results of STM observations on how the substrate temperature affects the forming C_{60} island array. Each time 0.1 ML of C_{60} was deposited onto the surface held at a given temperature after which STM observations were immediately conducted without changing the sample temperature. Hereafter, C_{60} coverage is given in the units of the completed fullerite-like (111) layer, i.e., 1 ML = 1.15×10^{14} cm^{-2}. One can see in the STM images in Fig. 1a the following typical trend: the island density decreases with growing temperature, while the island mean size consequently increases. Quantitative temperature dependence of C_{60} island number density is presented by the Arrhenius plot in Fig. 1b. One can clearly distinguish two regions which differ in slope and indicate different regimes of island nucleation on the "cold" surface (at 110–140 K) and on the "hot" surface (at 160–240 K). These regimes are characterized by effective activation energies of 33 and 123 meV, respectively.

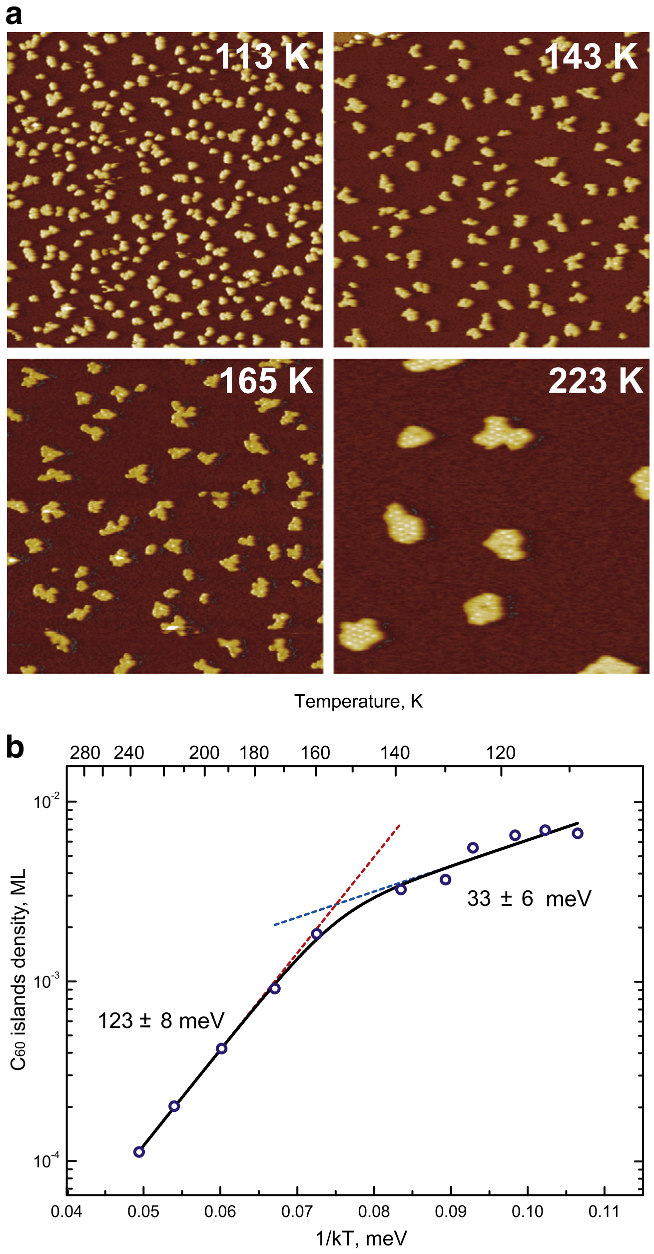

Fig. 1. (a) 200 × 200 nm^2 STM images showing C_{60} island arrays formed by depositing 0.1 ML onto Si(111)$\sqrt{3} \times \sqrt{3}$-(Au,In) surface held at various temperatures. (b) Arrhenius plot of C_{60} island number density. Dashed blue and red lines show the plots for low-temperature (110–140 K) and high-temperature (160–240 K) ranges, respectively; the sum of two exponents is shown by the black line.

To proceed further with evaluation of the diffusion parameters, one needs to establish a critical island size *i*. As one can see in Eq. (1), this