

Full length article

Scaling of size distributions of C₆₀ and C₇₀ fullerene surface islands

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ABSTRACT

We present experimental data and a theoretical analysis for the size distributions of C₆₀ and C₇₀ surface islands deposited onto In-modified Si(111) $\sqrt{3} \times \sqrt{3}$ -Au surface under different conditions. We show that both fullerene islands feature an analytic Vicsek-Family scaling shape where the scaled size distributions are given by a power law times an incomplete beta-function with the required normalization. The power exponent in this distribution corresponds to the fractal shape of two-dimensional islands, confirmed by the experimentally observed morphologies. Quite interestingly, we do not see any significant difference between C₆₀ and C₇₀ fullerenes in terms of either scaling parameters or temperature dependence of the diffusion constants. In particular, we deduce the activation energy for surface diffusion of $E_D = 140 \pm 10$ meV for both types of fullerenes.

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1. Introduction

Studies of island-size distributions (ISDs) and related features for different surface nanostructures, in particular fullerene islands [1–3], may help to understand and tailor collective properties of the island ensembles or extract the unknown kinetic parameters. In the limit of high ratios of the diffusion constant over the deposition rate, some island ensembles show the Vicsek-Family scaling behavior [4] within a range of deposition times (or surface coverages), where the ISDs in the scaling variables are independent of time. Particular form of the scaled ISD is determined by the island growth law and is paramount from fundamental viewpoint as well as for interpreting experimental results. The ISDs that satisfy the scaling hypothesis are usually studied within the irreversible growth models or with a time-independent critical size and appear much broader than in classical nucleation theory [5]. Herein, we present new data on the scanning tunnelling microscopy (STM) imaging of the ISDs of two-dimensional (2D) C₇₀ surface islands deposited onto In-modified Si(111) $\sqrt{3} \times \sqrt{3}$ -Au surface under different conditions and for different growth times. We then compare these data

with the previously obtained results for C₆₀ fullerenes and analyze both ISDs for the scaling behavior. Our analysis reveals the Vicsek-Family scaling property of the ISDs, whose universal analytic form allows us to deduce some physical constants and confirm nearly identical surface growth kinetics for both types of fullerenes. Most importantly, the particular scaling form of the ISDs suggests that the islands compete for a diffusion flux of fullerene monomers through the “hit and stick” aggregation mechanism in which the island boundary is random and the capture rates of monomers by differently sized 2D islands are proportional to the island surface area.

2. Experimental details

The experiments on the island growth of C₇₀ fullerenes were performed with an Omicron VT-STM installation operating in an ultrahigh vacuum ($\sim 2.0 \times 10^{-10}$ Torr). Atomically-clean Si(111) 7×7 surface was prepared *in situ* by flashing to 1280 °C after the samples were outgassed at 600 °C for several hours. Gold was deposited from an Au-wrapped W filament, indium from the Ta crucibles and fullerenes, C₇₀ (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-modified Si(111) $\sqrt{3} \times \sqrt{3}$ -Au

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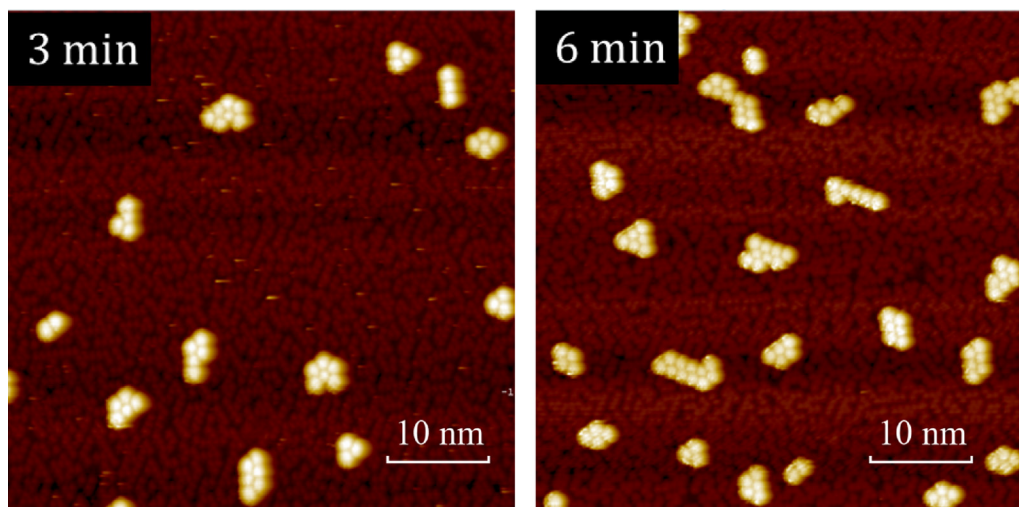


Fig. 1. Typical STM images of C_{70} surface islands taken at low temperature ~ 110 K after 3 and 6 min of growth (samples #5 and #6 in Table 1).

Table 1
Growth conditions of C_{70} clusters.

	Deposition time min	Growth temperature K	Coverage ML	Deposition rate ML/min	Cluster density nm^{-2}	Mean cluster size, number of C_{70} monomers
#1	10	112	0.02	0.002	0.007	3.56
#2	10 (5+5)	112	0.054	0.0054	0.011 ± 0.01	5.57
#3	5	112	0.03	0.006	0.0082 ± 0.0008	4.81
#4	10 (5+5)	112	0.059	0.0059	0.0104 ± 0.0002	6.71
#5	3	112	0.018	0.006	0.006 ± 0.001	3.29
#6	6	112	0.037	0.0062	0.008 ± 0.0007	5.09
#7	9 (6+3)	112–120	0.049	0.0054	0.0077	6.79
#8	8	120	0.06	0.0075	0.0055 ± 0.0006	11 ± 3
#9	12	120	0.068	0.0057	0.005 ± 0.001	13 ± 3

surface, the $\text{Si}(111)\sqrt{3} \times \sqrt{3}$ -Au surface was first formed by Au deposition onto $\text{Si}(111)7 \times 7$ surface held at 600°C and then ~ 0.5 monoatomic layer of In was deposited onto this surface held at room temperature (RT) followed by brief (~ 15 s) annealing at $\sim 600^\circ\text{C}$. Thus prepared In-modified $\text{Si}(111)\sqrt{3} \times \sqrt{3}$ -Au surfaces are highly ordered and homogeneous [5], in contrast to the pristine $\text{Si}(111)\sqrt{3} \times \sqrt{3}$ -Au surfaces which contain a dense network of random domain boundaries [6,7]. Since fullerenes are highly mobile on this surface, the C_{70} island growth occurs only at low temperatures of ~ 110 K. The island growth were studied in the range of C_{70} coverages from 0.02 to 0.08 ML. [One monolayer (ML) is defined as a close-packed hexagonal array of C_{70} molecules, $1 \text{ ML} = 1.155 \text{ nm}^{-2}$.] In each experimental run, the sizes of 700 to 2000 C_{70} islands were evaluated to obtain a reliable statistics. To avoid any post-growth effects, STM observations were conducted at low temperatures of ~ 110 K. Fig. 1 shows the typical STM images of C_{70} fullerene islands after 3 and 6 min of growth. The growth conditions, mean size and surface density of islands for different samples are summarized in Table 1. Note that all islands have one-monolayer thickness. The second-layer islands start to form when the C_{70} coverage becomes an order of magnitude higher, more than 0.8 ML [8].

3. Results and discussion

3.1. Size distributions

Our previous growth study of C_{60} fullerene surface islands revealed a discrepancy between the experimental and theoretical ISDs [1]. The mismatch may originate from a simplified theoretical model used in Ref. [1] which assumes size and coverage-

independent capture rates and hence does not account for a competition of the neighboring islands for the diffusion flux of monomers (in this case, single C_{60} fullerenes). In Ref. [9], a more comprehensive ISD has been obtained which is an asymptotic solution to the rate equations for irreversible homogeneous surface growth with size-linear and coverage-dependent capture rates. Size linearity of the capture rates in the mean field approximation applies to only a limited number of growth systems such as one-dimensional atomic chains [10] or vapor-liquid-solid nanowires growing by surface diffusion [11]. However, in the scaling limit of high ratios of the adatom diffusion constant D over the deposition rate $F, \Lambda = D/F \rightarrow \infty$, this feature is well-justified for large enough sizes and shows that larger islands have larger capture zones surrounding such islands and that the strength of a given island to capture monomers is roughly proportional to its surface area [12,13] (see, for example, Refs. [14–16] for a detailed review). Therefore, in this work we apply the model of Ref. [9] to a comparative study of the growth kinetics of C_{60} and C_{70} fullerene clusters and analyze the ISDs for the scaling behavior.

According to the Vicsek-Family scaling property in the limit $\Lambda \rightarrow \infty$ [2,9,10,12–17], the ISDs re-plotted in the scaling variables $(s^2/\Theta)n = f(s/s)$ (with n as the initial ISD, $\langle s \rangle$ as the mean size, Θ as the surface coverage and s as the size) are expected to collapse to a time-independent scaling function for all but very short times. The scaling shape then remains throughout the entire pre-coalescence stage of island growth. The scaling function $f(x)$ obtained in Ref. [9] has the form

$$f(x) = (p+1)b^{p+1} \frac{\Gamma(a-p)}{\Gamma(a+1)} x^p \gamma(bx, a-p) \quad (1)$$

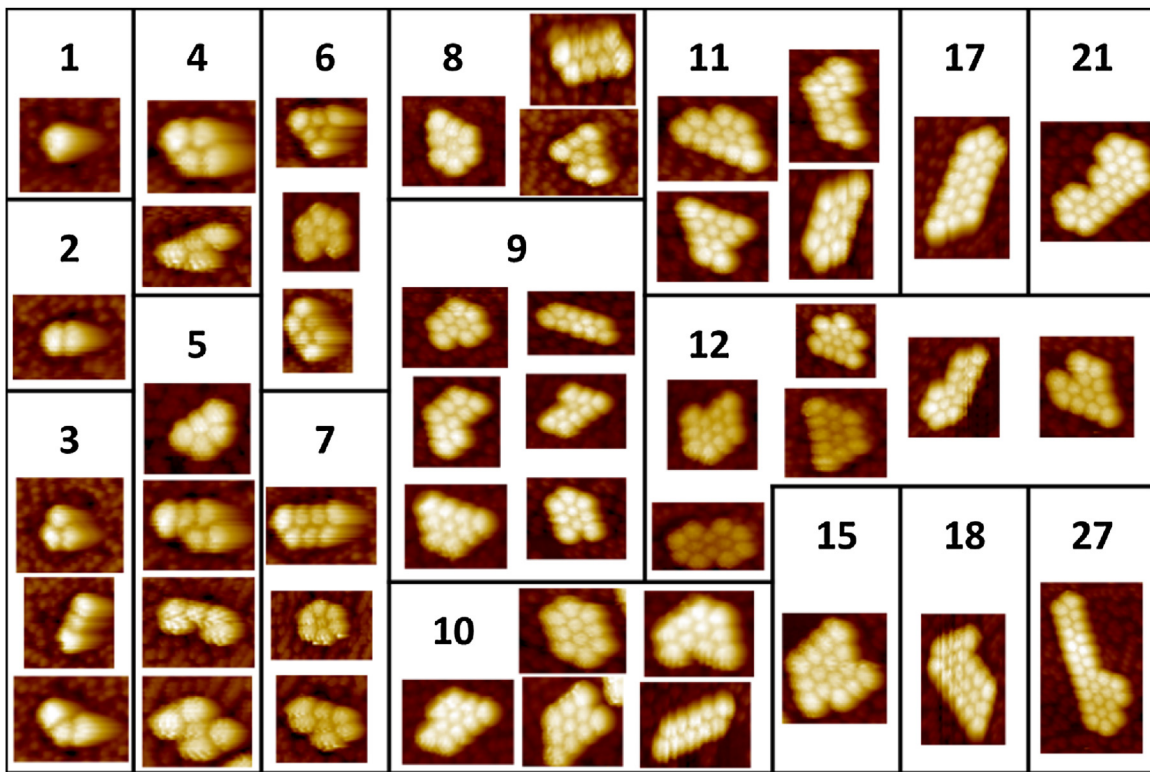


Fig. 2. STM images showing different shapes of differently sized C₇₀ islands, with the s numbers indicated for each image.

With

$$b = \frac{(a + 1)(p + 1)}{p + 2} \quad (2)$$

Here, $\Gamma(q)$ and $\gamma(y, q)$ denote the gamma-function and the regularized upper incomplete gamma-function, respectively. This $f(x)$ depends on the two parameters a and p which define the size and coverage-dependent capture rates $\sigma_s(\Theta)$ according to

$$\sigma_s = c\Theta^p(a + s - 1), \quad (3)$$

meaning that the capture rate in our model is linear in size and a power-law function of the coverage. The c parameter does not enter the scaling function.

A number of publications demonstrate that kinetic Monte-Carlo (KMC) simulations reproduce very well the experimental results on the epitaxial growth of C₆₀ fullerenes [18–20]. Below we assume that C₆₀ and C₇₀ fullerene islands have similar a and p and refer to the results of KMC simulations which indicate a nearly linear dependence of the capture rates on the coverage in the case of “hit and stick” aggregation process [13]. Fig. 2 shows the shapes of differently sized C₇₀ islands with no preferred 2D geometry, supporting the assumption of “hit and stick” aggregation. This implies that $p=1$ in our case, as for fractal islands in Ref. [13]. When the island size is much smaller than the capture zone and the sticking probability is close to 1.0, the shape of the islands should not strongly affect the growth rates and hence the resulting SDs. Fig. 3 shows that the scaled SDs for both types of fullerenes C₆₀ and C₇₀ follow quite nicely the scaling function given by Eqs. (1) and (2) with $p=1$, where the only fitting parameter a extracted from the best fit equals 6.3.

The greatest deviations around the peak position ($s \sim 1$) are seen for samples #1 and 5. Both samples refer to the low C70 doses, i.e. to the very early stage of the island formation. At this stage, the effect of the surface defects (which might act as heterogeneous nucleation centers) can be substantial. Although the defect density in

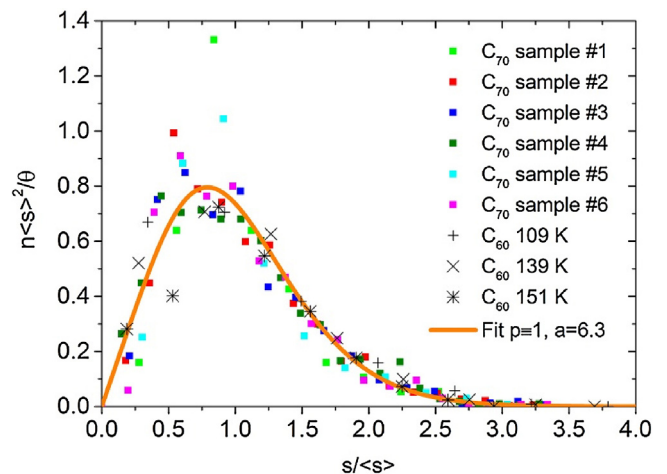


Fig. 3. Scaled size distributions of C₆₀ [1] and C₇₀ fullerene surface clusters: experimental data for different samples (symbols) and the analytic scaling function given by Eqs. (1) and (2) at $p=1$ and $a=6.3$ (line).

the present experiments is typically very low, the island density in the beginning of growth is also low and hence possible contribution of heterogeneous nucleation may lead to the observed dispersion of the data points near the peak position of the scaled ISD.

3.2. Mean island size

According to the result of Ref. [9], the mean island size is proportional to the surface coverage

$$\langle s \rangle = k(a, p)(c\Lambda)^{\frac{1}{p+2}} \Theta, \quad (4)$$

where $k(a, p) = (p + 1)(a + 1)(p + 2)^{-\frac{p+1}{p+2}} a^{\frac{1}{p+2}}$. Clearly, the k factor depends only on a and p and hence is the same for C₆₀ and C₇₀.

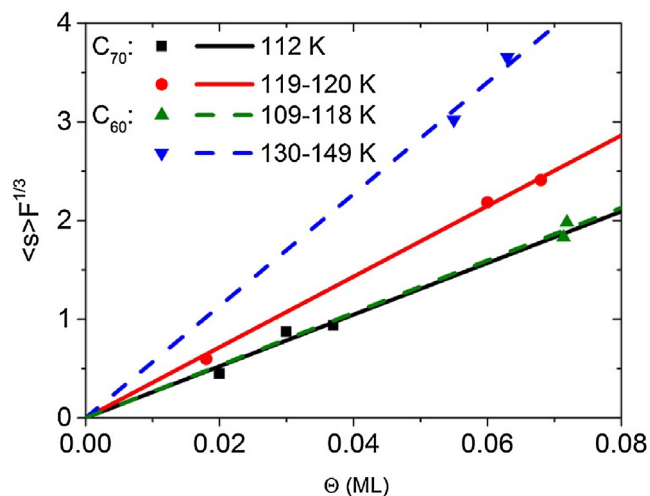


Fig. 4. Scaled mean sizes of C_{60} and C_{70} fullerene islands at different temperatures versus the coverage: experimental data for different samples (symbols) and linear dependences obtained from Eq. (5) (lines).

Therefore, we can evaluate the $c\Lambda$ and cD values from the analysis of the coverage dependences of the mean size. For $p=1$, this dependence can be put in the form

$$\langle s \rangle F^{1/3} = \text{const} \times (cD)^{1/3} \times \Theta \quad (5)$$

for different deposition rates F . Fig. 4 shows a good agreement of the linear dependences of $\langle s \rangle F^{1/3}$ on the coverage with the available experimental data points. Furthermore, by analyzing the slopes of the lines at different temperatures, the diffusion constants of both types of fullerenes follow the same Arrhenius-type dependence $cD = A \exp\left(-\frac{E_D}{kT}\right)$, with $E_D = 140 \pm 10$ meV and $A = 3.6 \times 10^9 \text{ nm}^{-2}/\text{min}$. The obtained value of the activation energy for surface diffusion is very close to the previous result of Ref. [1], where the deduced E_D value was 137 meV for C_{60} fullerenes.

4. Conclusions

We have shown that the scaled ISDs of both C_{60} and C_{70} fullerene surface islands obtained after different growth times and under different conditions are well fitted by the analytic scaling function which has a form of a power law times an incomplete gamma-function. The a and p parameters of the scaled ISD equal 6.3 and 1, respectively, in all cases. This supports the scaling hypothesis of high surface diffusivities of the fullerene monomers with respect

to their deposition rates as well as the linear size and coverage dependences of the capture rates. We observe almost no difference between the C_{60} and C_{70} growth kinetics and find the activation energy for surface diffusion of both C_{60} and C_{70} monomers of about 140 meV for temperatures between 112 and 120 K. Therefore, both types of fullerenes demonstrate *qualitatively* similar assembly properties. Overall, identical parameters of the scaled ISDs for C_{60} and C_{70} fullerenes on In-modified $\text{Si}(111)\sqrt{3} \times \sqrt{3}$ -Au surface suggest that the scaling property is intrinsic for this system and should hold within a wider range of growth conditions and deposition times, with a possible extension to other substrates. These generalizations will be in focus of our further research and will be reported elsewhere.

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