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Impurity Decoration for Crystal Shape Control: C_{60} on Ag(111)

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The decoration of hexagonal Ag/Ag(111) monolayer islands by chains of C_{60}, observed via STM at 300 K, dramatically changes the nanocrystalline shape and fluctuations of the islands. We tune coverage so that a single chain of C_{60} fully decorates each Ag island boundary, forming a closed circular ‘‘necklace.’’ We model the C_{60}-induced rounding in terms of competing energetic and entropic effects. We thereby characterize the decorated-step fluctuations and estimate the C_{60}-Ag and C_{60}-C_{60} attractions to be ~ 0.13 and ~ 0.03 eV, respectively. Generalizations of our model show that decorating molecules of both circular and rectangular surface-projected symmetry will similarly lower the energy of fully kinked boundaries, leading to corner rounding and reorientations by 30° on (111) surfaces and 45° on (100) surfaces.

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The attachment of trace amounts of impurities to a crystal can radically change its symmetry, shape, and stability [1–7]. One common way this occurs is via decoration of surface steps. Since steps make up a minute fraction of the surface area, relatively few impurities are sufficient for full decoration. This alters step dynamics, which in turn can lead to significant and sometimes unexpected changes in surface morphology. A well-documented example involved the temperature-dependent 60° reorientation of Pt/Pt(111) monolayer islands [1] caused by as little as 10^{-3} monolayers of CO. Such sensitivity to impurities is beautifully exploited in nature. In cold-water fish, for example, antifreeze proteins arrest the growth of ice crystals in the blood by decorating crystal steps. This produces large hexagonal pits in the basal plane of the crystal that are rotated by 30° with respect to the surrounding hexagonal plane face [3]. In humans, too, the growth of kidney stones can be controlled by the adsorption of citrate, a urinary molecule that induces rounding of stepped hillocks on the crystal surface [4].

In this Letter, we examine how step decoration affects crystal morphology by studying Ag/Ag(111) monolayer islands decorated by chains of C_{60} molecules (see Fig. 1). We focus on the decoration of the edges (steps) of 2D crystals (islands) to assay the effect of interface symmetry, e.g., the orientation dependence of C_{60} attachment, allowing an analytic description of the induced island-shape change. This work complements the more usual treatments of step decoration and/or nanowire formation on vicinal surfaces, which by design only consider attachment to steps having a single orientation [8].

The celebrated Wulff construction [9,10] is routinely used [11,12] to relate the measured equilibrium shapes of undecorated islands to the orientation dependence of the step line tension $\beta(\theta)$, or free energy per length, where θ is the local angle of a step relative to a close-packed direction. In turn, functional forms for $\beta(\theta)$ can be derived using lattice-gas models [10,13,14]. Generalizing this procedure to include decorated steps is challenging, largely due to the wide range of possible symmetry combinations. To date, most attempts have been computational in nature [15] or have focused exclusively on steps in a single, usually high-symmetry direction [16]. Here, guided by STM observations, we introduce an analytic bond-counting model that includes entropic effects and can self-consistently describe the observed orientation-dependent C_{60} attachment to Ag(111) steps, allowing us to estimate the C_{60}-Ag and C_{60}-C_{60} interaction energies. Generalizations of the model elucidate how decoration can alter crystal shape and symmetry depending on the bonding symmetry of the decorating species and underlying substrate.

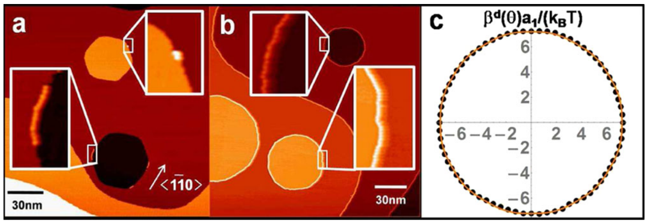

FIG. 1 (color online). At 300 K, Ag(111) monolayer adatom (orange or gray) and vacancy (black) islands are hexagonal. (a) Deposited C_{60} (light dots highlighted in insets) initially decorates the corners of islands. (b) C_{60} coverage is tuned so the islands are fully decorated, and their equilibrium shape becomes circular. (c) Fit of the experimental dimensionless line tension $\beta^d(\theta)a_1/(k_BT)$ (black dots) to Eq. (1) (solid line). The experimental data come from a fluctuating C_{60} decorated island averaged over 66 sequential topography STM images [17].

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As described previously [17,18], C_{60} molecules were evaporated onto clean Ag(111) surfaces held at 300 K. STM measurements reveal that at low concentrations, C_{60} molecules adsorb and migrate to the lower edges of steps. For closed steps bounding bare hexagonal adatom and vacancy monolayer islands, C_{60} molecules preferentially nucleate and form short chains near the island corners, along the fully kinked step directions, analogous to initial decoration of high-curvature regions joining close-packed, straight steps [19]. As the chains grow, the island corners round until the chains converge and form a complete, single-strand C_{60} "necklace" [20]. The fully decorated adatom and vacancy islands become circular, as shown in Fig. 1, indicating that the C_{60} step-edge attachment sufficiently favors kinked orientations of the boundary to change the overall shape of the nanoscale island. These observations suggest the following hierarchy of interaction energies: First, the C_{60} molecules must be attracted to the Ag step (with bond energy ϵ^{AC}) more than to each other (bond energy $\epsilon^{CC} < \epsilon^{AC}$); otherwise they would form clumps at the step edge before fully decorating it. Second, the Ag atoms must be attracted to each other more than to the C_{60} ($\epsilon^{AA} > \epsilon^{AC}$); otherwise the molecules would tend to penetrate the step.

To describe the system, our model consists of a (111) step with macroscopic length L and orientation $0 \le \theta < \pi/6$ (symmetry giving other angles), as shown in Fig. 2(a). The step is fully decorated by a single strand of spherical molecules, with the close-packed unkinked portion oriented at $\theta = 0$ and the fully kinked portion oriented at $\theta = \pi/6$. The substrate step Cartesian coordinates are $(M, N) \equiv (L/a_1)(\cos\theta, \sin\theta)$, where a_1 is the nearest-neighbor distance between step atoms ($a_1 \approx 2.89$ Å for Ag). As in the experiment, we assume the temperature ($\sim$300 K) is low compared to the attractive nearest-neighbor bond energy ϵ^{AA} between step atoms ($\epsilon^{AA} \approx$ 234 meV for Ag [21]). In this case, undecorated steps spend most of their time in ground state configurations, with all kinks geometrically forced rather than thermally activated. Steps with the same macroscopic length L and orientation θ then have the same number of kinks. As these kinks rearrange themselves (sometimes into higher-order kinks), steps fluctuate among degenerate states. When these steps are decorated, their energy $E_0 \approx \epsilon^{AA}(M + N/\sqrt{3})$ (the sum of broken ϵ^{AA} required to form the step) and entropy [22]

$$g_0 \approx \binom{M + N/\sqrt{3}}{2N/\sqrt{3}}$$

are reduced by the bonds formed with the C_{60}.

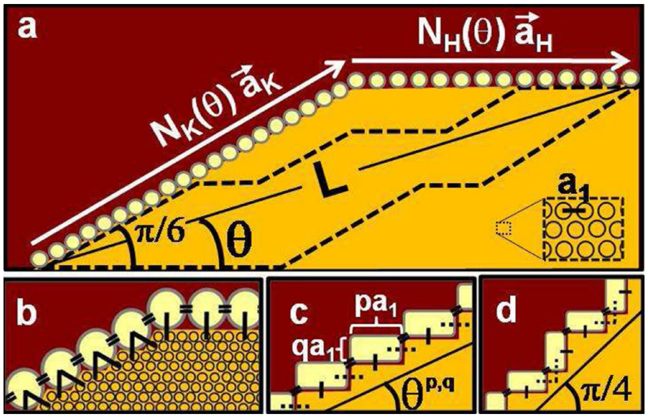

FIG. 2 (color online). (a) Viewed from above, a (111) step separates an upper terrace (orange or gray) from a lower terrace (red or dark gray). The step is decorated by molecules (light circles) and has macroscopic orientation θ and length L. At low temperatures, N_H molecules decorate the unkinked portion of the step ($\theta = 0$) and N_K decorate the kinked portion ($\theta = \pi/6$). The decorated-step edge is microscopically traced out by vectors summing to $N_K\vec{a}_K + N_H\vec{a}_H$. Two degenerate steps are shown as dashed black lines. (b) Microscopic model for C_{60} decorating a Ag(111) step with the C_{60}-C_{60} spacing fixed at the nearest-neighbor separation (with $|\vec{a}_K| = |\vec{a}_H|$). Along the fully kinked direction, C_{60} is in registry with Ag (small circles) double kinks. (c),(d) Microscopic models for decoration of (100) surfaces by molecules of rectangular symmetry (light rectangles) with dimensions $(p, q)a_1$, where p and q are integers and step-molecule bond strengths are assumed proportional to the length of molecule in contact with the step. (c) Decoration along the $\theta = \theta^{p,q}$ direction. (d) Decoration along the $\theta = \pi/4$ fully kinked direction maximizes the bond strength per macroscopic length.

Because the substrate step is anisotropic, there are two types of step-molecule bonds: N_H bonds of energy ϵ^H, between molecules and unkinked portions of the step, and N_K bonds of energy ϵ^K, between molecules and kinked portions of the step. For molecules with isotropic interactions like C_{60}, $\epsilon^K > \epsilon^H$ since kinks can rearrange themselves into higher-order kinks [e.g., the double kinks in Fig. 2(b)] to maximize molecular contact. The number of these higher-order kinks is geometrically fixed, as discussed above. The decorated-step energy is thus $E_0^d = E_0 - N_K\epsilon^K - N_H\epsilon^H$. The number of each type of bond is $N_K = 2Na_1/|\vec{a}_K|$ and $N_H = (M - N\sqrt{3})a_1/|\vec{a}_H|$, where $\vec{a}_K$ and $\vec{a}_H$ are vectors that connect nearest-neighbor molecules along kinked and unkinked portions of the step, respectively. The step edge is now traced out by a series of vectors: $N_H\vec{a}_H + N_K\vec{a}_K$. Different combinations of these vectors trace out degenerate steps, two examples being the dashed black lines in Fig. 2(a). The decorated-step entropy is therefore

$$g_0^d = \binom{N_H + N_K}{N_H}.$$

Together with E_0^d, we can now write the low-temperature (111) decorated-step line tension $\beta^d(\theta) \approx (E_0^d - k_BT\ln g_0^d)/L$, valid for $0 \le \theta < \pi/6$:

$$\beta^d(\theta)a_1 = E_0a_1/L - \epsilon^K n_K - \epsilon^H n_H - k_BT\ln\left[\frac{(n_K + n_H)^{n_K+n_H}}{(n_K)^{n_K}(n_H)^{n_H}}\right], \qquad (1)$$

where $(n_K, n_H) \equiv (N_K, N_H)a_1/L$. Here we have taken the thermodynamic limit ($L \rightarrow \infty$) and used Stirling's approximation for $\ln g_0^d$.

A similar argument holds for (100) steps, the only difference being the angle of the kinked portion of steps in Fig. 2(a) changes from $\pi/6$ to $\pi/4$. Then, $E_0 \rightarrow \epsilon^{AA}(M+N)/2$ [10], $N_K \rightarrow (N\sqrt{2})a_1/|\vec{a}_K|$, and $N_H \rightarrow (M-N)a_1/|\vec{a}_H|$. With these adjustments, Eq. (1) is valid for $0 \leq \theta < \pi/4$.

Much as a surfactant lowers surface tension [23], the molecular interactions lower the step line tension. Depending on the strength of ϵ^K compared to ϵ^H (for a given $|\vec{a}_K|$ and $|\vec{a}_H|$), the *anisotropy* of the line tension also changes, in turn causing changes in the equilibrium island shape. When this occurs, the decorating molecules behave as morphactants [2]. Upon decoration, kinked steps are favored energetically, but pay a higher entropy penalty since they loose more degrees of freedom as higher-order kinks form. As ϵ^K increases compared to ϵ^H, the two effects produce island rounding. Eventually energy dominates and kinked steps become thermodynamically preferred, causing islands to reorient themselves, as shown in Fig. 3. Decoration can therefore make surfaces either more or less isotropic.

Within this framework, we can now account for the Ag(111) island-shape change caused by decorating C_{60}. To do so, we fit Eq. (1) to the experiment. Since the C_{60} are uniformly spaced around the island [17], $|\vec{a}_H| = |\vec{a}_K| \approx 1$ nm. Using the Wulff construction, the experimental orientation-dependent line tension can be extracted from the measured equilibrium island shape, viz., radius R as a function of polar angle ψ:

$$\beta^d(\theta) \propto \frac{R^2(\psi)}{\sqrt{R^2(\psi) + \dot{R}^2(\psi)}}, \tag{2}$$

where $\dot{R} \equiv \partial R/\partial \psi$ and step orientation $\theta = \psi - \tan^{-1}(\dot{R}/R)$ [24]. In our case, the analysis is especially simple since $R(\psi)$ is nearly a perfect circle, with absolute magnitude of the line tension $\beta^d(\theta) \approx 65$ meV/Å [17]. Fitting this to our model [see Fig. 1(c)] yields $\epsilon^K \approx 0.29$ eV and $\epsilon^H \approx 0.16$ eV.

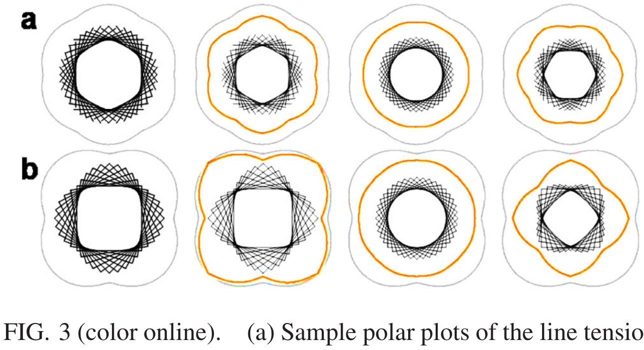

FIG. 3 (color online). (a) Sample polar plots of the line tension of an undecorated (111) step (light gray line) in comparison to the decorated-step line tension (orange or gray line) and corresponding equilibrium island shape (enclosed by scaled black Wulff-construction lines), with $|\vec{a}_K| = |\vec{a}_H| = 2a_1\sqrt{3}$, for increasing values from left to right of $\epsilon^K/\epsilon^H = 1.3$, 1.8, and 2.2. The leftmost plot shows the undecorated line tension and island shape. (b) The same for a (100) step, with $|\vec{a}_K| = 2a_1\sqrt{2}$, $|\vec{a}_H| = 2a_1$ and $\epsilon^K/\epsilon^H = 3.0$, 7.3, and 10.

This analysis reveals C_{60} favors steps over the terrace by ~0.23 eV (the average of ϵ^K and ϵ^H). Once attached to steps, C_{60} prefers kinked portions by an additional ~0.13 eV ($\epsilon^K - \epsilon^H$). This is consistent with the Smoluchowski effect [25], where the lower edges of steps are electron rich, making kinked regions especially favorable to C_{60}—known electron acceptors. To gain further insight, we consider the microscopic decorating geometry. Since the C_{60} are uniformly spaced around the islands, we know ϵ^K and ϵ^H share a component coming from nearest-neighbor bonds ϵ^{CC} between C_{60}. Also, along the fully kinked direction, Ag can form double kinks that have a length $2\sqrt{3}a_1 \approx 9.98$ Å, comparable to the spacing between two abutting C_{60} molecules [18]. As depicted in Fig. 2(b), each C_{60} molecule can then form approximately two bonds of energy ϵ^{AC} with Ag step edge atoms along kinked regions, rather than just one bond along unkinked regions. Based on these considerations, we decompose the bond energies as follows: $\epsilon^K = 2\epsilon^{AC} + \epsilon^{CC}$ and $\epsilon^H = \epsilon^{AC} + \epsilon^{CC}$. Solving gives $\epsilon^{AC} \approx 0.13$ eV and $\epsilon^{CC} \approx 0.03$ eV. Reassuringly, these interactions satisfy the expected hierarchy of energies, with $\epsilon^{AA} > \epsilon^{AC} > \epsilon^{CC}$.

The general use of Eq. (1) and the model shown in Fig. 2(a) require $\epsilon^K > \epsilon^H$. Although this should hold for spherical or circular molecules with which kinks can maximize contact, molecules with other symmetries might well not prefer the kinked direction. E.g., on a (100) surface, rectangular molecules with dimensions roughly $(p, q)a_1$, where p, q are integers, ostensibly prefer steps with mean angle $\theta^{p,q} \equiv \tan^{-1}(q/p)$, as shown in Fig. 2(c). Surprisingly, as Fig. 2(d) demonstrates, the fully kinked direction ($\theta = \pi/4$) is still preferred, since an appropriate rearrangement of geometrically forced kinks along this direction is energetically more favorable for all positive p and q; only when $p = q$ (square molecules) is attachment the same. [A similar result holds for (111) steps.] Thus, Eq. (1) and Fig. 3 remain applicable, suggesting decoration-induced island-shape change occurs broadly [26].

This picture of the C_{60} decoration energetics also elucidates the experimental observations of thermal decorated-step fluctuations [17]. Mysteriously, decorated Ag islands fluctuate with a distinctly different kinetic signature from undecorated islands [17] (nonconserved vs conserved, respectively), although previous work has shown that the presence of C_{60} does not hinder the motion of Ag atoms along the step edge [18]. This is surprising because the bonds ϵ^{AC} formed between the C_{60} and the step edge should correlate their fluctuations. To investigate this further, we fit the experimentally measured histogram of angles ϕ formed by triads of neighboring C_{60} molecules decorating an island [17]. Here the data have been binned

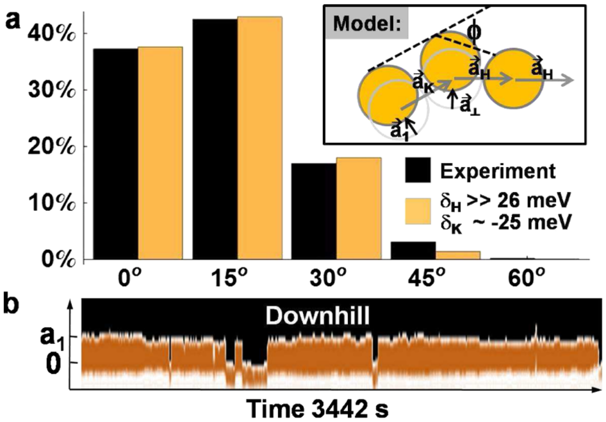

FIG. 4 (color online). (a) The experimental histogram [17] (black bars) of angles ϕ formed by three neighboring C_{60} molecules decorating a step compared to a theoretical histogram based on an extension of the decorating model (inset). The best fit (orange or gray bars) suggests that C_{60} decorating kinks can randomly hop towards the step an amount a_1. (b) STM measured displacement of a decorating C_{60} molecule (brown or gray) as a function of time. The lower, downhill terrace is black.

around the observed peaks at multiples of 15°, as shown in Fig. 4(a). The peaks at 15°, 45°, and 60° offer a clue, since our current model accounts only for $\phi = 0°$ and 30°. A simple extension of our model attributes these additional angles to C_{60} "hops" perpendicularly away from kinked or unkinked portions of the step by an amount $a_1/a_\perp$ at an energy cost $\delta_{K/H}$, where $2a_\perp/\sqrt{3} = a_1$, as shown in the diagram in Fig. 4(a). The local character of the hops is confirmed by measurements of the temporal motion of a single C_{60} molecule, shown in Fig. 4(b). Using Boltzmann weights for the probability of observing the angular configurations of Fig. 4(a), we find $\delta_H \gg 26$ meV (i.e., insurmountable at 300 K), while $\delta_K \approx -25$ meV. Thus, C_{60} molecules decorating kinked portions of steps appear to occasionally hop a single Ag unit cell toward the step, consistent with Fig. 4(b).

Based on this evidence, the thermal motion of the C_{60} seemingly has a vibrational part (the hops of amplitude a_1) that is weakly coupled to the adjacent Ag step edge. The nonconserved nature of these hops is consistent with the measured "dispersion relationship" of the decorated-step fluctuations, where the time constant $\tau_\lambda \propto \lambda^2$ [17] (where λ is the fluctuation wavelength). This contrasts starkly with underlying Ag steps, where $\tau_\lambda \propto \lambda^4$, indicating conserved, step-edge-diffusion kinetics. This difference can be explained by the model since Ag edge-atoms must rapidly diffuse along the step-edge as the decorated step moves between degenerate ground states. This converts double kinks to single kinks and attracts the decorating C_{60}, randomly inducing "hops" towards the step.

In conclusion, we have constructed a model allowing us to characterize the Ag(111) island-shape change induced by decorating C_{60} molecules and thereby estimate both the Ag-C_{60} and C_{60}-C_{60} interaction energies. This kind of analysis should prove useful for exploiting step decoration by C_{60} [8,27] and other molecules [28], where the growth and stability of self-assembled structures are sensitive to the ratio of molecule-molecule and molecule-step interactions. The model is easily extended to other surfaces or molecular symmetries and could also be extended to 3D, where dramatic nanocrystal shape changes affect catalysis [6]. Finally, when combined with *ab initio* programs or continuum theory, the model should enable *predictions* of decorated island shapes and thereby promote the engineering of surface morphologies.

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