Stress relaxation via the displacement domain formation in films of C$_{60}$ on Ge(100)

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The initial stages of the C$_{60}$ film growth on Ge(100) have been studied using scanning tunneling microscopy, low-energy electron diffraction, and molecular-dynamics simulation. A gradual transformation of the surface-mediated rhombic superlattice of C$_{60}$ on Ge(100) into a bulk close-packed crystal is observed with the increasing thickness of the film. The transformation is accompanied by a formation of specific surface defects in a shape of walls oriented along one of the two unit vectors of the C$_{60}$ superlattice and forming an angle of $\sim 70^\circ$ with each other. The crystalline lattices at opposite sides of the wall are shifted by a nonintegral lattice vector with respect to each other, forming displacement domains. The molecules belonging to a wall occupy saddle-point positions above two neighboring molecules in the underlying monolayer. A pair of intersecting walls is coupled to an edge dislocation located at the top angle between them. We show that the displacement domain formation is similar to a commensurate-incommensurate transition in adsorbate-substrate systems, and that it provides a mechanism for the stress relaxation in the growing film.

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INTRODUCTION

Following the discovery of fullerene molecules, numerous studies focused on the growth of C$_{60}$ films on different substrates.\(^1\)\(^-\)\(^15\) Thick monolayers of C$_{60}$ of the order of 10–20 ML have been found to develop a close-packed (cp) face-centered-cubic lattice independently from the initial structure of the C$_{60}$ adlayer.\(^1\)\(^-\)\(^15\) The transformation of C$_{60}$ films into a bulk solid has been observed to proceed abruptly at a certain thickness of a C$_{60}$ film, and to break it into separate crystalline islands.\(^4\)\(^-\)\(^8\)

The unique property of C$_{60}$ films on Ge(100) is that they transform into a bulk lattice continuously, in contrast, to films of C$_{60}$ on a structurally similar Si(100) substrate.\(^15\) In this paper we address the mechanisms of the stress relaxation and the defect structure that enable such a continuous transformation.

EXPERIMENT

The experiments are performed in an ultrahigh-vacuum chamber ($p = 5 \times 10^{-11}$ torr), equipped with a homemade scanning tunneling microscope (STM),\(^4\) a cylindrical mirror analyzer for Auger electron spectroscopy (AES), a low-energy electron-diffraction (LEED) unit and a differentially pumped ion gun. The 0.5-mm-thick wafers of Ge(100) ($\rho = 0.2$ $\Omega$ cm) cut into $8 \times 12$ mm$^2$ pieces are used as substrates for C$_{60}$ depositions. They are cleaned by Ar$^+$-ion bombardment at oblique incidence, annealed via direct current heating at 750 $^\circ$C, and, following these procedures, show a sharp (2$\times$1) LEED structure and no impurities in AES spectra. STM studies of the substrate surface reveal 500–800-Å-wide terraces composed of dimer rows of Ge atoms. The dimer rows are oriented either parallel or perpendicular to the terrace edges, and their orientations alternate at each consecutive terrace. C$_{60}$ molecules are deposited from a well-outgassed Knudsen cell on a freshly prepared substrate while it is cooled down from $\sim 100–150$ $^\circ$C to 30–40 $^\circ$C. The thickness of a C$_{60}$ film is calibrated using AES and the STM.

RESULTS

A. Low-energy electron diffraction

The LEED pattern of a single-monolayer film of C$_{60}$ on Ge(100) [Fig. 1(a)] shows a fourfold symmetry associated with the 90$^\circ$ rotation of the substrate lattice on consecutive terraces.\(^12\) The reconstruction of the LEED pattern is presented in Figs. 1(b) and 1(c). We start with a single-domain pattern [Fig. 1(b)] corresponding to a single orientation of the substrate lattice. The (2$\times$1) diffraction spots of the substrate are shown with large circles. The elementary vectors of the C$_{60}$ superlattice (in reciprocal space) contribute a rectangle of spots in the center of the pattern, and are marked with crosses in Fig. 1(b). Other spots arise from multiple elastic scattering of electrons on the adsorbate and substrate, and their positions are derived by adding one or two lattice unit vectors of C$_{60}$ to a vector of the substrate. The experimentally observed pattern is reconstructed in Fig. 1(c) by superimposing two single-domain patterns rotated by 90$^\circ$ with respect to each other.

The sum of the lattice unit vectors of the C$_{60}$ lattice coincide precisely with a half-order spot of Ge(100), indicating commensuration of two lattices in the direction perpendicular to dimer rows [Figs. 1(a)–1(c)]. Along the dimer rows the C$_{60}$ lattice is incommensurate with that of the lattice of Ge. For comparison, Fig. 1(d) shows the ideal diffraction pattern of a commensurate 3$\times$4 superlattice of C$_{60}$ on Ge(100). The 1$\frac{1}{2}$- and 2$\frac{1}{2}$-order spots in this pattern fall on the same line in contrast to the experimental LEED pattern. [Figs. 1(a) and 1(c)]. Careful measurements of the spot positions show that...
the distance between molecules occupying the same row is 3.5% shorter than three lattice constants of the substrate.\(^{12}\)

The evolution of the LEED pattern with the increasing thickness of the C\(_{60}\) film is shown in Fig. 2. At 3 ML [Fig. 2(b)] the pattern exhibits streaks connecting spots that are broadened compared to a 1-ML film [Fig. 2(a)], and have a triangular shape. The streaks are enhanced in a LEED pattern of a 5.5-ML film at the expense of vanishing spots [not shown], and develop into 28 partially unresolved spots in the LEED pattern of a 10-ML film [Fig. 2(c)]. Twenty four of these spots are grouped in 12 pairs, and create a central ring inside the ring of four Ge half-order spots. Four of these 12 pairs are located in a close proximity to half-order spots of Ge, and create triangles with them.

The first monolayer spots transform into radial streaks, and are still present in a LEED pattern of a 10-ML film. One spot in each of eight remaining pairs falls on such a streak. The angle between the spots in a pair is \(\alpha = 9.5^\circ \pm 0.5^\circ\), and corresponds to the angle between differently oriented domains. The angle between the adjacent pairs of spots is \(\beta \approx 30^\circ\), indicating the formation of rotation domains with a close-packed lattice.

**B. Scanning tunneling microscopy**

The STM study of submonolayer and monolayer films of C\(_{60}\) on Ge(100) has been reported elsewhere.\(^{12}\) Here we briefly summarize the results of this study. C\(_{60}\) molecules fill troughs between dimer rows of Ge atoms, and form a rhombic lattice which is schematically shown in Fig. 3. The long diagonal of the C\(_{60}\) unit cell is equal to two dimer spacings. The length of the short diagonal is equal to the distance between molecules occupying the same trough, and is controlled primarily by the interactions between C\(_{60}\)
molecules. The lattice of a C$_{60}$ monolayer on Ge(100) can be regarded as a uniaxially deformed cp lattice: its long diagonal is compressed and its short diagonal is expanded compared to the two-dimensional (2D) cp lattice of C$_{60}$ (16.00 Å vs 17.39 Å and 11.58 Å vs 10.04 Å, respectively). The intermolecular distance in the C$_{60}$/Ge(100) adlayer is shorter than in the fcc crystal (9.87 Å vs 10.04 Å).

The islands of the first monolayer nucleate at atomic steps and fill both upper and lower terraces from the edge inside the terrace. Beginning from the second monolayer, the nucleation of the top monolayer occurs in the middle of atomic terraces, presumably at defects.

The nucleation of the fourth monolayer occurs when the third monolayer fills most of the surface, and is consistent with the layer-by-layer growth mode. The uncovered areas of the second monolayer and small islands of the fourth monolayer account for less than 10% of the surface of the 3-ML film. The surfaces of the second and third monolayers exhibit 3D corrugations in a shape of narrow walls. Figure 4(a) shows an area of a 3-ML film containing such walls. The image is differentiated to reduce the contrast associated with the islands of the fourth monolayer of C$_{60}$ at the left and right edges of the image, and, thus, the walls are observed as pairs of black and white stripes. Practically all the walls in Fig. 4(a) are arranged in pairs inclined by an angle of 70° to each other. The length of a wall reaches 300–500 Å, and is comparable to the width of the atomic terrace on which it is located. The walls are elevated by 0.7–1 Å from the surface, and their full width at half maximum vary from 30 to 50 Å, as can be seen from their cross sections [Fig. 4(b)].

A white line in the center of the STM image shows an atomic step propagating to the surface. Figure 5(a) shows a high-resolution STM image exemplifying an area of contact of two walls in a 3-ML film. To clarify its structure, we extract molecular coordinates from Fig. 5(a), fill vacancies and invisible surface areas with molecules, and construct a two-dimensional ball model presented in Fig. 5(b). The invisible surface areas arise from C$_{60}$ molecules adsorbed on the top and from the defect of the STM image located in its lower part. The area with the particularly large number of invisible sites can be observed at the top angle between the walls. The coordinates of molecules in this area are extrapolated from the coordinates of
molecules in adjacent areas. We have filled the area between the walls with molecules to show that it contains an additional parallel row of molecules. The STM image shows that the walls do not intersect each other but are separated by a gap of 2–3 rows of molecules. One of the walls extends by ~5 intermolecular distances below the area of contact. The elevated part of a wall is formed by 4–5 molecular rows parallel to the lattice unit vectors, or, in short, by 4–5 parallel rows (likewise, we call a row of molecules aligned by diagonals of the unit cell a “diagonal row”). The surface enclosed by walls is also corrugated: each third or fourth parallel row protrudes above others by 0.4–0.7 Å, forming a wave of 5–6 periods.

Figure 5(b) also reveals that diagonal rows bend, traversing a wall. The sign of bending is opposite for walls oriented along different lattice unit vectors (vectors $a$ and $b$ in Fig. 5). To estimate the magnitude of the bend, we extract $x$ coordinates of molecules at two $y$ coordinates above and below the walls, respectively (see Fig. 5), and in Fig. 6 we plot the $x$ displacements between molecules above and below the walls. Note that the displacement reaches ~8.5 Å (i.e., approximately an interrow spacing), and is gradually accumulated from left to right of Fig. 5(a). Using the Burgers construction, we find that an additional parallel row of molecules is inserted at the top angle between the walls. The surface defect in Fig. 5 can be considered as a 2D analog of a dislocation, and as the initial stage of formation of an edge dislocation intersecting the surface. The core of a 2D dislocation is situated in the gap between the walls, and its Burgers vector [Fig. 5(b)] approaches the lattice unit vector and is parallel to the shorter of the two intersecting walls.

The relation between the lattice parameters in consecutive layers can be observed in Fig. 7, showing an edge of the third monolayer (light) and a portion of the uncovered second monolayer (dark). Figure 7(b) presents a ball model of the same image. The triangular protrusion of the third monolayer in the center of Fig. 7(a) is attached to an atomic step [a small part of it is observed in the upper right corner of Fig.

**FIG. 5.** (a) A STM image of a $350 \times 280$-Å² area containing two intersecting domain walls (the tip bias is +3.8 V, the electron current 80 pA). (b) A two-dimensional ball model of the image in (a): the vacancies are filled with molecules; the molecules belonging to the walls are marked with dots; the Burgers construction shows that the pair of intersecting walls is coupled to an edge dislocation; the Burgers vector of the dislocation is equal to a lattice unit vector, and is parallel to the shorter wall.

**FIG. 6.** The $x$-direction displacements between molecules occupying positions below and above the walls in Fig. 5.

**FIG. 7.** (a) A STM image of an edge of the third monolayer of C$_{60}$ (bright) with an emerging second monolayer (dark). The molecular lines at the right side of the triangular protrusion are aligned with those in the second monolayer. The molecular lines at the left side are misaligned by $1^\circ$–$2^\circ$, and form a wavelike structure ($250 \times 180$ Å², tip bias 4.5 eV, electron current 100 pA). (b) A ball model of (a); 23 vertical rows of the third monolayer cover 24 vertical rows of the second monolayer.
The right edge of the protrusion is straight, and is aligned with parallel rows of the second monolayer. The left edge, on the other hand, has a sawlike structure with parallel rows misaligned with those of the substrate by ~1–2°, indicating a lattice mismatch between the protrusion and the underlying monolayer lattice. A careful comparison shows that the lattice of the third monolayer is stretched in the horizontal direction in such a way that 23 vertical short-diagonal rows of molecules of the third monolayer are spread over 24 rows of the second monolayer.

The average angle between the lattice vectors \( \varphi \), measured in flat areas of the surface, reduces from 71.8° in the first monolayer to 71° in a second monolayer and 69.8° in the third monolayer (in each case, the corresponding monolayer is the topmost in the film).

At a 5.5-ML coverage, the surface continues to be filled layer by layer (Fig. 8), and its structure resembles that of the third monolayer but shows larger amplitudes of corrugations. The islands of the sixth monolayer have a shape of parallelogram or rhombus [Fig. 8(a)], and are composed of areas with a quasiperiodic wavelike structure and stripes of a relatively flat surface [Figs. 8(a) and 8(b)]. The wavelike structures consist of 3–6 periods each composed of 2–3 parallel rows.

Parallel rows of molecules in corrugated areas of the surface are misoriented with respect to those in adjacent flat areas of the surface. The angle between parallel rows in differently oriented wavelike structures is ~70°, while that in flat areas is 64.5°. The transition region between the flat and corrugated areas is continuous, and contains no dislocations, as can be observed in the lower left part of Fig. 8(b). Two adjacent parallel rows in a wavelike structure are shifted in such a way with respect to each other that they form a nearly rectangular pattern [Fig. 8(c)]. Thick films of C\(_{60}\) could not be studied using the STM because of their poor conductance.

C. Potential barriers for a single C\(_{60}\) molecule on the surface of a C\(_{60}\) film

We have performed static calculations of the binding energy of a single C\(_{60}\) molecule placed above different symmetry points of a 2D crystalline lattice of C\(_{60}\). Two geometries of the C\(_{60}\) lattice have been used. The first is a cp lattice, and the second is a distorted cp lattice of a C\(_{60}\) monolayer on (2 \( \times \) 1)Ge(100). The pair interaction between molecules is described by the Girifalco potential.\(^{17}\) The schematics in Fig. 3 show the location of the symmetry points including two local-energy minima (\( P_1 \) and \( P'_1 \)), a saddle point between second nearest neighbors (\( P_2 \)) and a saddle point between the nearest neighbors (\( P_3 \)). (Hereafter, we refer to molecules separated by the shorter diagonal of the lattice unit cell as to second nearest neighbors.) The results of the calculations are summarized in Table I. On the perfect cp lattice, the displacement of a C\(_{60}\) molecule from \( P_1 \) into \( P_2 \) or \( P_3 \) raises the molecule by 0.46 Å (\( \Delta z \)) above the surface plane, and decreases its binding energy by ~200 meV (\( \Delta U \)). On a rhombic lattice, because \( d_1 > a \) (Fig. 3), \( \Delta z \) and \( \Delta U \) values are lower for the displacement from \( P_1 \) into \( P_2 \) (\( \Delta z_1 = 0.16 \) Å and \( \Delta U_1 = 100 \) meV) and larger for the displacement from \( P_1 \) into \( P_3 \) (\( \Delta z_3 = 0.75 \) Å and \( \Delta U_3 = 250 \) meV).

D. Molecular dynamics simulation

To model the growth of a multilayer film, we have performed molecular dynamics simulation (MDS) using the well-known Verlet leap-frog algorithm.\(^{19}\) The latter enables an easy velocity rescaling which mimics thermalization of the system. C\(_{60}\) intermolecular interactions are calculated using the Girifalco potential\(^{17}\) with a cutoff radius (\( R \)) of 2.5 molecular diameters (i.e., \( R = 17.75 \) Å). The boundary conditions, particular to the problem, are as follows.

(a) The first monolayer of \( N = 50 \times 50 \) C\(_{60}\) molecules is bound at \( z = 0 \). The germanium substrate is represented by a rigid lattice. The interaction of the first monolayer of C\(_{60}\) molecules with the substrate is described by a harmonic potential, and its geometry is rigid apart from thermal fluctua-
TABLE I. The height and the potential energy of a C_{60} molecule placed above different symmetry points of a crystalline lattice of C_{60}, z_{1} is the height above P_{1}, z_{2} the height above P_{2}, and z_{3} the height above P_{3}, \( x_{1} = \frac{1}{2} d_{3} \), and \( U_{1}, U_{2}, \) and \( U_{3} \) are corresponding energies. \( \Delta X_{i} \) are differences between X values in points \( P_{i} \) and \( P_{j} \). All distances are in [Å] and energies in [eV]. The diagram in Fig. 3 shows the location of points \( P_{1}, P_{2}, \) and \( P_{3} \).

<table>
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<th>2D cp lattice of C_{60}</th>
<th>C_{60} on Ge(100)</th>
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<tr>
<td>( z_{2} )</td>
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<td>8.14</td>
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<td>( z_{3} )</td>
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</tr>
<tr>
<td>( U_{2} )</td>
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<tr>
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<td>0.16</td>
</tr>
<tr>
<td>( \Delta z_{13} )</td>
<td>0.46</td>
<td>0.75</td>
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The epitaxial growth of a van der Waals solid is accompanied by the transformation of a surface superlattice into a bulk cp crystal. The superlattice of C_{60} on Ge(100) can be regarded as a uniaxially deformed cp lattice, and the transformation of such a lattice into a cp crystal represents a rather general case. The deformation of the 2D cp lattice inevitably leads to the attractive interaction between second-nearest neighbors, which tend to rearrange the molecules into
FIG. 9. (Color) Molecular modeling of the $C_{60}$ film growth. Small black circles represent molecules of the first monolayer. Large colored circles represent molecules of the second monolayer. Those elevated by more than 8.66 Å above the first monolayer are shown in red. Most of these molecules occupy saddle points between nearest neighbors in the first monolayer and form type-1 walls. The molecules placed above the saddle point between second-nearest neighbors (green) form type-2 walls. Molecules occupying left ($P_1$) energy minima are shown in blue, those occupying right ($P_2$) minima in cyan. Arrows mark the diagonal rows of molecules used to measure the expansion of the lattice in the second monolayer compared to the first [Figs. 11(a) and 11(b)]. A frame shows a region with two intersecting walls which is extracted and analyzed in Fig. 12.

FIG. 10. The distribution of molecular $z$ coordinates in the second monolayer. The molecules contributing to the tail of $z$ distribution (i.e., $z>8.66\,\text{Å}$) form type-1 walls (see Fig. 9).

FIG. 11. The molecular shifts in the second monolayer with respect to the minima of the potential energy provided by the first monolayer. (a) Shift in the $y$ direction of a $y$ row. (b) Shift in the $x$ direction of an $x$ row.
other is comparable to the growth temperature potential barrier for the translation from one minimum to the other. Therefore, molecules easily adjust their position along the displacement domain formation in the gradual transformation of the lattice. The displacement domain formation, in turn, could be driven both by dynamic and kinetic factors. We start our consideration with dynamic factors, and, in particular, we consider if the formation of displacement domains could be predicted based on the minimization of the potential energy of the film.

The molecules of the top monolayer fill one of two symmetric energy minima in a unit cell (\(P_1\) or \(P'_1\) in Fig. 3). The potential barrier for the translation from one minimum to the other is comparable to the growth temperature (see Table I). Therefore, molecules easily adjust their position along the line connecting the energy minima. On the other hand, the molecular displacement of similar magnitude in the perpendicular direction (see Fig. 3) is hampered by a large variation of the potential energy. We assume that the interaction of molecules with the substrate is strong and the deposition of each consecutive monolayer does not affect much the structure of previous monolayers that remain intact with each other and with the substrate. (The rigidity of the film structure is also supported by a kinetic barrier, that prevents it from reconstruction). In this case, we can separate the potential energy of the top monolayer from that of the whole film, and consider the structural changes in the top monolayer as a commensurate-incommensurate transition in an adsorbate-substrate system (i.e., we consider the top monolayer as an adsorbate and the underlying molecular monolayer as a substrate).

Using the Girifalco potential, we calculate the potential energy of the top monolayer using the geometry of a monolayer of \(C_{60}\) on Ge(100), and compare it with the potential energy of a close-packed lattice. The interaction between nearest neighbors provides the main contribution into the potential energy (254 meV per bond) which is slightly lower than that in a close-packed lattice (277 meV per bond). Neighboring \(C_{60}\) molecules experience repulsive forces, which counterbalance the attractive forces between non-nearest neighbors. But, because the repulsive forces rise much faster with the deviation from equilibrium than attractive forces, the distance between nearest neighbors and their binding energy remain nearly constant. The only interaction, that vary significantly from one lattice to the other, is that between the second nearest neighbors (99.3 meV vs 277 meV). For a qualitative explanation, we can consider only this contribution, assuming that the interaction between nearest neighbors in adjacent monolayers is nearly constant. In this case, the problem of the energy minimization becomes quasi-one-dimensional.

The one-dimensional problem has been considered by Frenkel' and Kontorova\(^\text{20}\) using a simple model, in which adsorbed molecules are represented by masses attached to each other by springs and placed in a sinusoidal potential representing a substrate. For certain interaction parameters, the minimization of potential energy gives a "soliton" solution in which domains of commensurate phase (i.e., consisting of molecules occupying the minima of the sinusoidal potential) are separated by soliton walls representing an incommensurate phase (i.e., consisting of molecules displaced from the energy minima of the sinusoidal potential).\(^\text{20,21}\) Following the consideration suggested by Pokrovskiy and Talapov,\(^\text{21}\) we can make a rough estimation for the threshold parameters of a commensurate-incommensurate transition. For this purpose, we compare the energy of fully commensurate and fully incommensurate phases of a monolayer of \(C_{60}\) superimposed with the uniaxially deformed cp lattice of a \(C_{60}\) crystal. In a fully commensurate phase, molecules occupy the energy minima of the substrate potential, and the main component of the potential energy of the top monolayer is the attractive potential between second-nearest neighbors. In this case, the total energy of a domain is \(E = NU\), where \(U\) is the intermolecular potential in a commensurate lattice and \(N\) is a number of molecules in a domain. In a fully incommensurate lattice, the intermolecular distance corresponds to
a minimum of the intermolecular potential and molecules probe the lattice potential in random points. Therefore, the domain energy is: \( E = N V_m \), where \( V_m \) is the mean value of the lattice potential. Commensurate to incommensurate lattice transition and a soliton wall formation occurs if \( U > V_m \). \( U \) is equal to 0.18 eV for a given geometry, and \( V_m \) can be estimated as half of \( \Delta U \), that is, 0.12 eV (Table I). (In fact, only the molecules belonging to the walls acquire substantial potential energy. Therefore, \( V_m \) is inversely proportional to the linear dimensions of displacement domain.) Thus, within the precision of our estimation, the domain formation is energetically favorable, and the displacement domains can appear spontaneously in the top monolayer of \( C_{60} \).

The rhombic symmetry of displacement domains can also be explained by the potential-energy minimization. The reduction of the short diagonal of the lattice unit induces repulsive forces between nearest neighbors. Due to the fast rise of repulsive forces between molecules the intermolecular distance remains constant. This inevitably leads to the expansion of the long diagonal of the lattice unit. In Fig. 14, we present a superposition of two lattices with equal intermolecular distances and slightly different top angles between the lattice unit vectors. The displacement between the lattices is a periodic function of coordinates and has rhombic symmetry. The regions with the largest molecular displacements are marked by solid lines and correspond to type-1 walls. Vertical dashed lines mark type-2 walls.

The crystalline lattices of domains separated by a wall are shifted by a vector equal to the distance between two adjacent potential-energy minima (Fig. 3). Assuming that the crystalline lattice is nearly close packed, we find that the domains are shifted by \( 1/3a(211) \), where \( a \) is intermolecular distance.

The formation of displacement domains can also be explained by kinetic factors, i.e., by the nucleation at multiple sites separated by nonintegral lattice vectors. The division of the film into domains could be inherited from one monolayer to another, leading to their accumulation at progressive stages of growth. Even if the nucleation sites of \( C_{60} \) islands on a \( C_{60} \) surface were separated by large distances, it might arise from the nucleation of the first monolayer at atomic steps. The experimentally observed sizes of displacement domains correlate with the width of an atomic terrace on which they are observed indicating that the terrace dimensions could be a limiting factor for the domain growth as well [Fig. 4(a)]. On the other hand, according to our observations, the density of nucleation sites is much lower than the density of displacement domains in the film [Fig. 4(a)]. Thus, at least in 2–3-ML films, the characteristic sizes of domains could approach to their natural sizes, i.e., those of domains growing from a single nucleation center.

The lattice relaxation inside the domain can be understood from the following. Attractive interactions between second-nearest neighbors are in part counterbalanced by the lattice potential of the underlying monolayer. Therefore, the repulsion between nearest neighbors is reduced compared to that in the first monolayer. Hence the \( C_{60} \) lattice expands in the direction of the long diagonal of the lattice unit. Indeed, a 4% expansion of the long diagonal which corresponds to a \(-0.8^\circ\) decrease of the angle between the lattice vectors is observed in MDS. This decrease fits well the experimentally observed angle reduction from 71.8° in the first monolayer to 71° in the second monolayer and 69.8° in the third monolayer.

The assumption that the relative orientation of the lattice vectors in consecutive monolayers is symmetric with respect to the stress direction leads to a rhombic symmetry of molecular displacements in the film that determines the rhombic symmetry of the surface corrugation (Figs. 5 and 14). This kind of lattice relaxation produces tangential streaks in a LEED pattern connecting the first-order spots and the spots corresponding to the sum and difference of the lattice vectors [Fig. 2(c)]. If the rhombic symmetry was preserved at progressive stages of growth we would end up with close-packed domains of the same orientation, aligned with the stress direction. The streaks in a LEED pattern corresponding to the directions of the lattice unit vectors in the first monolayer [Fig. 2(c)] indicate that there exist a mechanism that preserves the alignment of the lattice vectors throughout the whole film at least in a part of it.

Previous observations of rotation domains in \( C_{60} \) films grown on various substrates also show such an alignment. The angle between rotation domains, as can be seen from Table II is practically equal to the difference between the \( C_{60} \) lattice angle in the first monolayer and 60°.

The formation of rotation domains is explained by the energetic advantage of rotational epitaxy. According to the theoretical analysis provided by McTague and Novaco and Fuselier, Raich and Gillis, as a first approximation, the

| \( C_{60} \)/Ge(100) | 9.5 | 11.8 |
| \( C_{60} \)/Si(100) (Ref. 15) | 15.8 | 18.0 |
| \( C_{60} \)/GaAs(110) (Refs. 6 and 29) | 7 | 10.4 |

FIG. 14. A simplified model of molecular displacements in two consecutive monolayers of \( C_{60} \). The lattice unit of the top monolayer is contracted along its short diagonal, and is stretched in the direction of its long diagonal while the intermolecular distance is kept constant as reflected in the symmetry of the Moiré pattern. The top monolayer molecules located above a pair of neighboring molecules in a previous monolayer are aligned along the lattice unit vectors. Solid lines mark the positions of type-1 walls, and dashed lines mark type-2 walls.
The molecules in each elevated parallel row form a nearly rectangular pattern with molecules in one of the adjacent parallel rows [Fig. 8(c)]. Such a rectangular pattern is characteristic for partial steps produced by stacking faults in the \((-111)\) plane intersecting the \((111)\) plane and were previously observed in fcc crystallites of C\(_{60}\) molecules on Si(100).\(^5\) The two-row periodicity of the pattern [Fig. 8(c)] indicates that each third layer of molecules in the \((-111)\) plane is missing, i.e., instead of \(ABABC\) stacking of \((-111)\) planes defining the fcc crystalline structure, \(ABAB\) stacking characteristic for hexagonal-close-packed (hcp) crystallites is observed.

The parallel rows in differently oriented stacking faults form an angle of \(\sim 70^\circ\) with each other that exceeds the angle between the lattice unit vectors in flat areas of the film. The orientation of parallel rows in stacking faults coincides with the lattice unit vectors of the first monolayer.

The fact that rotation domains appear only at high coverage suggests that they rather gradually develop within the old phase than are formed via a phase transition. A possible explanation for such a gradual formation of displacement domains involves preferential nucleation of the top monolayer at type-1 walls which is observed in MDS (Fig. 13). The walls are oriented roughly in the same direction as the lattice unit vectors of the first monolayer of C\(_{60}\). This explains the streaks in a LEED pattern of a 10-ML film in places of the first monolayer spots.

The transformation of a surface-mediated superlattice of C\(_{60}\) on Ge(100) into a bulk crystal at progressive stages of the film growth is gradual, and compatible with the layer-by-layer growth. This transformation is driven by attractive forces between the second-nearest neighbors in a uniaxially deformed cp lattice and is similar to a commensurate-incommensurate transition in adsorption systems. The resulting structure of the film involves displacement domains separated by solitonlike walls. At high coverage (>8 ML), rotation domains of bulk crystallites of C\(_{60}\) are observed. Their creation and alignment are explained by the preferential nucleation of the top monolayer at domain walls. The structure of the stacking fault defects indicates the coexistence of fcc and hcp stacking in the films.

**CONCLUSIONS**

The transformation of a surface-mediated superlattice of C\(_{60}\) on Ge(100) into a bulk crystal at progressive stages of the film growth is gradual, and compatible with the layer-by-layer growth. This transformation is driven by attractive forces between the second-nearest neighbors in a uniaxially deformed cp lattice and is similar to a commensurate-incommensurate transition in adsorption systems. The resulting structure of the film involves displacement domains separated by solitonlike walls. At high coverage (>8 ML), rotation domains of bulk crystallites of C\(_{60}\) are observed. Their creation and alignment are explained by the preferential nucleation of the top monolayer at domain walls. The structure of the stacking fault defects indicates the coexistence of fcc and hcp stacking in the films.

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15D. Klyachko and D. M. Chen (unpublished).

16The intermolecular distance is well determined for bulk crystals of C\(_{60}\) and is equal to 10.04 Å; see Ref. 15.


22In two-dimensional systems, the molecular positions with respect to potential wells are correlated. This correlation expectedly increases the value of \(V_m\) by forcing molecules out of the local-energy minima, and, therefore, reduces the critical value of the
interaction between molecules required for a commensurate-incommensurate transition.

The position of the energy minima of a single C\textsubscript{60} molecule above a monolayer of C\textsubscript{60} can be calculated rather precisely from geometrical considerations (see Fig. 3). Let us assume that this molecule forms a tetrahedra with three molecules in a monolayer and that its distance from all of them is equal to \( a \), which is also the distance between the nearest neighbors. A simple calculation gives a distance from the energy minima to the larger side of the triangle:

\[ P_1P_2 = \frac{2a^2 - d_1^2}{2\sqrt{4a^2 - d_1^2}}. \]

For the geometry of our experiment, \( a = 9.87 \text{ Å} \), \( d_1 = 11.58 \text{ Å} \), and \( P_1P_2 = 1.88 \text{ Å} \).

This is quite different from molecular interactions in the first monolayer. As we mentioned above, C\textsubscript{60} molecules fill the troughs between the substrate dimer rows and can easily diffuse along them. Attractive interactions between second-nearest neighbors, in this case, are compensated for mainly by repulsive interactions between nearest neighbors. As a result of that, the intermolecular bond is contracted.

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