Epitaxial growth of C\textsubscript{60} on highly oriented pyrolytic graphite surfaces studied at low temperatures

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Abstract

Graphite surfaces interact weakly with molecules compared to other conducting surfaces, bringing the molecule–molecule interaction to the foreground. C\textsubscript{60} on highly oriented pyrolytic graphite is a model system for studying the molecular self-assembly on surfaces. Our scanning tunneling microscopy measurements at liquid nitrogen temperatures confirm the previously observed island growth mode. Our results indicate that there is an epitaxial relationship of the molecular islands and the substrate with three possible orientations of the islands. For one of these orientations, we determine this epitaxial relationship by analyzing in detail an image taken across a C\textsubscript{60} island step edge. In this image we have obtained high-resolution on both the molecular island and the substrate. The result of this analysis is confirmed by two-dimensional Fourier analysis.

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(Some figures may appear in colour only in the online journal)
decrease leads to an angular smearing in the observed orientations [17].

We have studied the growth of C_{60} on the HOPG surface using scanning tunneling microscopy (STM) at liquid nitrogen (LN_{2}) temperatures. We have found three possible orientations of the islands with respect to the substrate. We have obtained atomic resolution on HOPG and molecular resolution on C_{60} within the same image. In this image we show that for a particular island there is an epitaxial relationship to the substrate. Two-dimensional Fourier transformation of high-resolution STM images supports this result.

2. Experimental

We used an approximately 3 × 13 mm²-sized piece of HOPG (grade H) with a mosaic spread of 3.5° ± 1.5° (Optigraph GmbH). The HOPG sample was mounted on top of a Si(111) stripe that served as heater. The HOPG was cleaved in air and degassed at T = 420 − 470 K in ultra-high vacuum (UHV). The surface quality of the substrate was checked with low temperature STM prior to the molecule deposition, for details see supporting information, available online at stacks.iop.org/NANO/30/025703/mmedia. All STM experiments were performed in a low temperature STM (LT-STM, Omicron) at LN_{2} temperatures in UHV. After checking the cleanliness of the HOPG surface, the substrate was transferred to an additional chamber of the system, the deposition chamber, and was thermalised in a room-temperature environment for 30 min. The C_{60} was deposited using a simple home-built evaporator. The evaporator consisted of a boron nitrate crucible that was heated by a stripe of tantalum foil. For evaporation the substrate was placed in front of the crucible at an angle of approximately 30°. We applied a constant current of I = 16.4 A to the Ta-heater of the crucible and the amount of C_{60} was controlled by varying the heating time between 1 min 30 s and 3 min. For the first 1 min 30 s the amount of deposited C_{60} remained negligible. After the pressure had recovered, typically within 2–3 min, the sample was directly transferred to the pre-cooled STM. For STM imaging the constant current mode was used for the distance controller. For some images, the tunneling current set point was varied during image acquisition as detailed below.

3. Results and discussion

Figure 1 shows a typical LN_{2}-STM image of the HOPG surface after deposition of a small amount of C_{60} molecules leading to a low coverage. Single molecular layer high C_{60} islands cover roughly 5% of the scanned surface. In most aspects the images agree well with previous STM studies [13, 15–17]. The islands are preferentially arranged at step edges [4, 6, 14, 17]. This preference for the growth at step edges is probably related to the high mobility of the C_{60} on the graphite surface [17], and is in contrast with the absorption of C_{60} on stronger interacting surfaces such as Pb/Si(111) [18] where C_{60} typically nucleates at surface defects on terraces.

Line defects attributed to subsurface HOPG defects are not decorated by C_{60}. The single molecular layer islands show hexagonally oriented edges with rounded corners. Three distinct types of C_{60} islands marked by the numbers 1 to 3 are found depending on the preferred orientations of their edges, which are indicated by white lines in the image. See text for details.
the island edges form a 120° angle with respect to each other as it would be expected for perfect hexagons. Type $3'$ denotes a variant of type $3$ obtained through a mirror symmetry of the type $3$ islands with the mirror oriented along the $y$-axis of the image.

Shin et al [17] performed a detailed computational (Novaco–McTague) analysis of the orientation of the island’s edges and found that 0°, 8°, and 29.9° are stable orientations for the growth of C$_{60}$ on HOPG. However, their low-energy electron-diffraction and STM measurements only found a slight preference for the 30°-orientation. They explained this preference by the preference for the C$_{60}$ islands to nucleate and align at step edges [17] which are oriented at 30° relative to the graphite lattice. Comparing these results to our data (see figure 1 and figure 2(a)), we identify type 1 and type 2 islands with the structures observed at a 0° and 29.9°. Type 3 and $3'$ islands respectively, although observed at an angle of 14°, could be tentatively identified with the 8°-structure within the experimental precision.

Upon increasing coverage, both, the size and the number of the islands increase as shown in figures 2(a) and (b). For higher coverage islands additionally nucleate and grow on the terraces and not only at step edges. Probably the new nucleation centers correspond to residual impurities or defects on the surface [14]. In previous studies on graphene grown on 6H-SiC(0001), a substrate that also interacts weakly with C$_{60}$, the collective movement of small fullerene islands has been reported as a consequence of the interaction with the STM tip.
The authors have observed that the islands that were not pinned by a defect showed a much faster mass transport. In our case larger islands for increasing coverage often show flower-like shapes instead of hexagonal ones, compare e.g.

figures 2(a) and (b). The flower-like shape is most likely the result of the coalescence of several hexagonal islands due to the large coverage (static coalescence [15]).

For increasing coverage also a second and higher layers grow on top of the single molecular layer high C_{60} islands discussed above. In figure 2, we observe that the first layer, grown on HOPG, shows a compact growth while the second layer, grown on C_{60}, shows a fractal-dendritic growth in agreement with literature [15, 16]. This is caused by a strong difference of the C_{60} diffusion barrier between the HOPG substrate (E_{B} = 13 meV) and the C_{60} island surface (E_{B} = 168 meV), suppressing step edge diffusion in the second layer, as suggested in [15, 16, 20]. No indications of dewetting are observed. On insulator surfaces, in contrast, the C_{60} molecules preferentially form a second layer and a peculiar island shape is caused by dewetting, such as in KBr (001) [6] and CaF2 (111) surfaces [5]. If the deposition time is increased further, the amount of layers and also the size of the layers both increase. Further measurements with variable substrate temperature during deposition should be performed to fully cover the dynamics of the growth.

After analyzing the shape of the islands, we now concentrate on their internal structure. In figure 2(c) we show an enlarged STM image with molecular resolution of the region A marked with a square in figure 2(b). The C_{60} island shows several defects labeled with arrows: D indicates two positions where a single C_{60} molecule is missing in the top layer. A slightly brighter molecule is marked with E. The defect E could be caused by a defect in the HOPG surface, by a modified C_{60} or by stress released due to the lattice mismatch between the C_{60} and the HOPG surface. Figure 2(d) shows a line profile measured along the line tagged B in figure 2(b). The apparent height of the first layer is roughly h_{1} = 1.5 nm. The apparent height measured with STM strongly varies in the literature between h_{1} = 1.05 nm and h_{1} = 1.88 nm [13–15]. In some cases, the large values are explained by an initial bilayer growth [14], while the low values of h_{1} have been attributed to electronic effects [15]. Here, we assume a single molecule height. The deviation might be explained by imprecisions of the scanner calibration since we also measure an increased height for HOPG steps. HOPG steps appear a factor of about 1.5 higher in our images compared to literature. However, the calibration has been previously double-checked at liquid He temperatures on other surfaces such as Ag(111) and Nb(110) and appears to be precise [21]. Therefore the deviation of the measured height for HOPG and C_{60} layers on HOPG is most likely to be attributed to electronic effects of the surface and the measured voltage, since these materials are not simple metals. In addition, the influence of the electronic state of the tip has an influence on the STM measurements. The apparent height of the second layer is approximately h_{2} = 1.2 nm.

To investigate the epitaxial relationship between the first layer of the C_{60} island and the substrate, we have performed high-resolution imaging at the area denoted as C in figure 2(b) comprising an edge of a type 1 island. The image shows molecular and atomic resolution on C_{60} and HOPG, respectively within the same image. U_{B} = 1.5 V, I_{T} = 20 pA. A representation of the height values alternating five times between black and white has been chosen in order to show the high-resolution contrast, both, on the upper terrace of the C_{60} island as well as on the HOPG substrate within the same image. Evaporation time 2 min 30 s. Inset: magnification of the C_{60} layer, marked with the white square.

Figure 3. High-resolution STM image at the area denoted as C in figure 2(b) comprising an edge of a type 1 island. The image shows molecular and atomic resolution on C_{60} and HOPG, respectively within the same image. U_{B} = 1.5 V, I_{T} = 20 pA. A representation of the height values alternating five times between black and white has been chosen in order to show the high-resolution contrast, both, on the upper terrace of the C_{60} island as well as on the HOPG substrate within the same image. Evaporation time 2 min 30 s. Inset: magnification of the 2 \times 2 nm^{2} area marked with the white square.
Figure 4. 2D-FFT analysis of molecularly and atomically resolved STM images. (a) STM image of the C$_{60}$ island in the center of figure 2(b). Scan size 500 × 500 nm$^2$, $U_b = 2$ V, $I_t = 20$ pA. The region marked in blue corresponds to the area shown in figure 3, where we simultaneously obtained molecular an atomic resolution. (b) Area marked with an empty white square in (a) on the C$_{60}$ island, 50 × 50 nm$^2$, $U_b = 2$ V, $I_t = 20$ pA. (c) Area marked with a filled white square in (a) on the HOPG surface, 10 × 10 nm$^2$, $U_b = 1.3$ V, $I_t = 50$ pA. (d) 2D-FFT data of image (b) obtained on the C$_{60}$ island, the main symmetry directions are marked in black. (e) 2D-FFT data of image (c) obtained on HOPG, the main symmetry directions are marked in orange. (f) Comparison of the main symmetry directions of the C$_{60}$ island and the HOPG substrate.
performed high-resolution imaging of an area fully covered by C₆₀, figure 4(b), and on the HOPG substrate, figure 4(c), with molecular and atomic resolution, respectively. The corresponding 2D-FFT data are shown in figures 4(d) and (e). The high symmetry directions of the C₆₀ lattice are marked in black and those of the HOPG surface in orange. Combining these two sets of directions in figure 4(f), we measure an angle of 34° between them. The deviation of this angle with respect to the above-mentioned 30° lies within the experimental error. The STM images have different sizes and different scanning speeds, they are differently affected by residual drift effects along slow and fast scanning axes possibly leading to small changes of the measured angles.

In literature the surface energy has been used as a measure of the molecule-substrate interaction in order to compare the formation of C₆₀ islands on wide-band gap insulators [7]. Due to the important molecular mobility, kinetic barriers can be overcome at the temperature at which the islands are formed. This also applies to HOPG substrates, where the weak van-der-Waals interaction favors island mobility [16, 19]. The idea has been put forward that low surface energy materials show dewetting in contrast to high surface energy materials [7]. This idea relates to the well-known general considerations that growth modes depend on the surface and interface energies [22]. C₆₀ shows dewetting for KBr [4], the insulator surface with the lowest surface energy available in that study (141 mJ m⁻² [7]), while it shows wetting on CaCO₃(1014) with a much higher surface energy (590 mJ m⁻²[7]). On graphite, even though graphite has an even lower surface energy compared to KBr (54.8 mJ m⁻² [23]), C₆₀ shows wetting comparable to the observations on CaCO₃(1014). This observation suggests that the surface energy alone cannot fully describe the interaction of molecules with a surface. The detailed nature of the interaction, e.g. whether the substrate is a metal or an insulator, or potentially the interaction energy of the molecule with the surface should be considered rather than the surface energy of the substrate alone. It appears that the surface energy of the substrate is only a well-chosen parameter if the same type of materials are considered, e.g. for comparison of different ionic crystalline surfaces.

4. Conclusion

We have investigated the growth of C₆₀ on HOPG using STM at liquid nitrogen temperatures. For low coverage C₆₀ single molecular layer islands grow in the form of hexagonally oriented edges with rounded corners decorating HOPG step edges. Upon increasing the coverage flower-like shape islands also grow on terraces, and multilayers appear showing a fractal-dendritic shape. In contrast to previous results, in our study we find three different orientations of the islands’ edges as predicted by theory. The remarkable stability of the islands have permitted further investigations. For one particular island, we have studied the epitaxial relationship with the substrate by analyzing a high-resolution image across an island edge where we have obtained molecular and atomic resolution within the same image. A 2D-FFT analysis of STM images on this region confirms that the symmetry directions of the C₆₀ islands and the HOPG surface form an angle of approximately 30°.

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