Nucleation and growth of C\textsubscript{60} overlayers on the Ag/Pt(111) dislocation network surface

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Abstract. We have investigated the room temperature growth of C\textsubscript{60} overlayers on the strain-relief dislocation network formed by two monolayers of Ag on Pt(111) by means of scanning tunneling microscopy. Extended domains of highly ordered dislocation networks with a typical superlattice parameter of 6.8 nm have been prepared, serving as templates for subsequent C\textsubscript{60} depositions. For low C\textsubscript{60} coverages, the molecules decorate the step-edges, where also the first islands nucleate. This indicates that at room temperature the C\textsubscript{60} molecules are sufficiently mobile to cross the dislocation lines and to diffuse to the step-edges. For C\textsubscript{60} coverages of 0.4 monolayer, besides the islands nucleated at the step-edges, C\textsubscript{60} islands also grow in the middle of terraces. The C\textsubscript{60} islands typically extend over several unit cells of the dislocation network and show an unusual orientation of the hexagonally close-packed C\textsubscript{60} lattice as compared to that found on the bare Ag(111) surface. Whereas C\textsubscript{60} grows preferentially in a \((2 \sqrt{3} \times 2 \sqrt{3})\) \textit{R}30\textdegree structure on Ag(111), on the Ag/Pt(111) dislocation network the C\textsubscript{60} lattice adopts an orientation rotated by 30\textdegree, with the close-packed C\textsubscript{60} rows aligned along the dislocations which themselves are aligned along the Ag<1-10> directions. For higher coverages in the range of 1-2 monolayers, the growth of C\textsubscript{60} continues in a layer-by-layer fashion.

1. Introduction
The ability to control the assembly of molecular species into complex supramolecular structures is of great importance for the future of molecular electronics and is attracting more and more attention. To realize this control on solid surfaces, there are two basic mechanisms that can be exploited. One is based on tuning the molecule-molecule interactions by an appropriate functionalization of the molecular building blocks. For instance, one-dimensional and two-dimensional (2D) supramolecular aggregates have been selectively created by proper functionalization of the porphyrin building blocks [1] on the herringbone reconstruction [2] of the Au(111) surface. Another example for this approach is the 2D molecular honeycomb network which has been formed by assembling two complementary species of molecules [3] on the \(\sqrt{3} \times \sqrt{3}\) \textit{R}30\textdegree Ag [4] on Si(111) surface. The second approach to control molecular assemblies aims at exploiting molecule-substrate interactions for a controlled anchoring of molecular building blocks. A promising choice are patterned substrates with a periodicity of a few nanometers, such as vicinal Au(111) surfaces [5]. On Au(11 12 12), the combination of discommensuration lines derived from the herringbone reconstruction [2] on small Au(111) terraces with regular steps leads to the formation of a rectangular 2D template surface [5], on which a 2D long-range ordered superlattice of C\textsubscript{60} nanochains perfectly replicating the template periodicity has been achieved [5].
In this study, we investigate the second mechanism mentioned above by using a quasi atomically-flat template surface which is formed in heteroepitaxy by the deposition of two monolayers (ML) of Ag on Pt(111). The stress induced by the 4.3% lattice mismatch of this bi-metallic system is relieved through the formation of a dislocation network [6-8]. The Ag(2ML)/Pt(111) strain-relief pattern has allowed to successfully fabricate well ordered 2D superlattices of small metal islands [8]. Up to now, however, there have been no reports on the use of such dislocation network templates to control the assembly of molecules. In this work, we report on the room-temperature (RT) adsorption of C\textsubscript{60} on Ag(2ML)/Pt(111) dislocation network surfaces. An unusual orientation of the molecular C\textsubscript{60} film is found, which is rotated by 30° compared to the (2\sqrt{3} × 2\sqrt{3}) R30° structure previously reported on the bare Ag(111) surface where the C\textsubscript{60} close-packed rows are aligned along Ag<11-2> [9-12]. On Ag(2ML)/Pt(111), the C\textsubscript{60} close-packed rows follow the same directions as the template dislocations lines, i.e. along Ag<1-10>.

2. Experimental

The experiments were conducted in two independent multi-chamber ultra-high vacuum (UHV) systems, both equipped with facilities for surface preparation, i.e., Ar\textsuperscript{+} ion sputtering and resistive sample heating. One system is equipped with an OMICRON RT scanning tunneling microscope (STM)/atomic force microscope, a combined set-up for X-ray and ultraviolet photoelectron spectroscopy (XPS/UPS) and low energy electron diffraction (LEED). The second system houses an OMICRON low temperature (LT) STM, used in the present study at 77 K, and a LEED. STM tips were mechanically cut from a Pt/Ir wire. Our Pt(111) single-crystal was first cleaned by several cycles of 1 keV Ar\textsuperscript{+} sputtering at RT and subsequent heating at 1120 K. For the last cycle, the Pt(111) substrate was exposed to Ar\textsuperscript{+} sputtering at 1120 K. In order to achieve Ag(2ML)/Pt(111) dislocation networks with long-range order, Ag (coverage ~ 2 ML) was first deposited on Pt(111) kept at RT and then annealed to 800 K [6-8]. Surface cleanliness and order of Pt(111) and Ag(2ML)/Pt(111) were checked by XPS, UPS, LEED and STM. C\textsubscript{60} molecules were sublimated from a resistively heated stainless steel crucible while the Ag(2ML)/Pt(111) substrate was maintained at RT.

3. Results and discussion

The Stranski-Krastanov heteroepitaxial growth of Ag on Pt(111) has been examined in detail by Brune et al. (see Refs. [6-8] and Refs. therein). It has been shown that the first ML of Ag wets the Pt(111) surface and grows pseudomorphically on it. Upon deposition of the second Ag layer, a dislocation network is formed to release the 4.3% compressive strain. It is not clear, however, if the dislocations are present in the topmost Ag layer or are buried in the first Ag layer on the Pt(111) substrate.

Figure 1a shows an STM image of a Ag(2ML)/Pt(111) dislocation network produced by the procedure outlined above. The dark lines aligned along the Ag<1-10> directions represent dislocations. As can be seen, the dislocation lines delimit three types of domains. Brune et al. [6] have proposed that the hexagon-delimited domains contain Ag atoms in face-centered cubic (fcc) stacking, while in the triangle-delimited domains (hcp1 and hcp2 in Figure 1a) the Ag atoms are in hexagonal close-packed (hcp) stacking. Figure 1b displays two height profiles both measured along the direction indicated in Figure 1a. The red curve of Figure 1b is from the STM image of Figure 1a, which was measured with a sample bias of −2 V and a set-point current of 2 nA, whereas the blue curve is from another STM image (not shown) of the very same position but imaged with a sample bias of −0.1 V and a set-point current of 1 nA. As can be seen from the line profiles, the change of one order of magnitude in the tunneling resistance does not change significantly the topographic profile, which can then be considered as a representation of the real corrugation of the template surface. From the profiles of Figure 1b one can see that the maximum corrugation of the dislocation network is about 40 pm. The centers of the fcc, hcp1 and hcp2 domains are measured within 10 pm at the same height, where the center of the fcc domain is typically measured as highest point. The center of the hcp1 domain is 8-12 pm lower compared to the fcc, and the center of the hcp2 domain somewhere in between. The lowest point of the pattern is the point where the hcp1 and hcp2 domains touch and is typically 40 pm below
the center of the hcp1 domain. The second lowest feature is the dislocation line between the hcp1 and the fcc domains with a depth of typically 25 pm. Much less pronounced is the dislocation line between the hcp2 domain and the fcc domain with a depth of 10 pm. It is worth to notice that these corrugation values are much lower as compared to a stepped surface, in the sense that the maximum slope of the STM topography \( \Delta z/\Delta x \) is of the order of 3% for the dislocation network, whereas at a step we typically measure 50%. In this respect, the dislocation line represents a structure which is 15 times less steep than a monoatomic step.

Even if not rigorously regular as is evident from Figure 1a, the Ag(2ML)/Pt(111) dislocation network has an average period of about 6.8 nm and can be regarded as a \((24 \times 24)\) superstructure (as \(24 \times a_{Ag}/\sqrt{2} = 24 \times 2.89 = 6.9\) nm is close to 6.8 nm). The dislocation network induced hexagonal superstructure was also attested in LEED patterns (not shown here) by the presence of extra diffraction spots around those of the Ag(111) lattice. In our case, such dislocation networks can extend over large areas, more than 100 nm x 100 nm, with only a few imperfections or defects.

**Figure 1.** (a) Topographic LT-STM image (40 nm x 40 nm, -2 V, 2 nA) showing a well-ordered Ag(2ML)/Pt(111) dislocation network. Appearing as dark lines aligned along Ag<1-10> are the dislocations, which separate fcc from hcp (1 and 2) domains. (b) Height profiles traced on the Ag(2ML)/Pt(111) pattern. The red curve corresponds to the red line indicated in the STM image (a) and the blue curve is from the same surface position but on another STM image measured with parameters (-0.1 V, 1 nA) different from those of (a).

Figure 2 shows a series of large scale (500 nm x 500 nm) STM images for different C\(_60\) coverages deposited at RT on freshly prepared Ag(2ML)/Pt(111) surfaces. For 0.08 ML C\(_60\) (Figure 2a), all molecules are adsorbed at the steps in the form of linear chains and small 2D islands. This indicates (i) the high mobility of the C\(_60\) molecules at RT \([5,9,10,13,14]\), (ii) the much more favorable C\(_60\) adsorption at the steps compared to the bare terraces \([5,9,10,13,14]\) and (iii) the ability of the molecules at RT to cross several dislocation lines. For 0.4 ML C\(_60\) coverage displayed in Figure 2b, the step-edges are fully decorated by C\(_60\), and large 2D islands are present on the upper and lower terrace of the step-edges. However, there is also a large number of C\(_60\) islands which are nucleated on the bare terraces and which are not in contact with step-edges. These islands have a diameter which ranges between 20 nm and 70 nm. From their size it is clear that the islands extend over several unit cells of the underlying dislocation network and therefore cover fcc, hcp1 and hcp2 domains. In between the large C\(_60\) islands, some individual C\(_60\) molecules and small C\(_60\) aggregates can be found. Closer inspection reveals that smaller aggregates are often pinned to defects (vacancy type) in the
dislocation network. On the other hand, individual C_{60} molecules are usually not located at an apparent defect, but rather on the fcc domains and close to one of their six corners (Figure not shown). At 0.9 ML C_{60} coverage (Figure 2c) most molecules contribute to the formation of the first ML. However, a layer-by-layer growth is initiated at the step-edges by occasional 2D second layer islands exhibiting a dendritic shape. In the first C_{60} ML no islands are present any more, but voids in an otherwise complete layer. At last for 1.3 ML C_{60} (Figure 2d) the first ML is closed and the 0.3 ML C_{60} excess forms dendritic islands in the second ML, which are not only nucleated from the step-edges but also in the middle of terraces. From the series of C_{60} coverages, we can conclude that due to their high mobility at RT, the C_{60} molecules grow in the two ML range in a layer-by-layer fashion on Ag(2ML)/Pt(111), as previously reported on Ag(111) and Au(111) surfaces [9]. From the comparison of the LEED pattern of the 1.3 ML C_{60} film (shown as inset in Figure 2d) and LEED patterns of the Ag(2ML)/Pt(111) substrate (not shown here) one can deduce that the C_{60} layers form a 2D hexagonally close-packed structure where the close-packed rows (that we note C_{60}<10>) are predominantly oriented along the Ag<1-10> directions. This is in clear contrast to what has been observed on the Ag(111) surface without dislocations, where the C_{60} layer takes a (2√3 × 2√3) R30° superstructure with the C_{60}<10> direction rotated by 30° with respect to Ag<1-10> [9-12].

Figure 2. Topographic STM images (500 nm x 500 nm) from different C_{60} coverages deposited at RT on Ag(2ML)/Pt(111): (a) 0.08 ML, (b) 0.4 ML, (c) 0.9 ML and (d) 1.3 ML. The inset of Figure 2.(d) shows the corresponding LEED pattern (32 eV). ((a,c,d) are RT measurements, (b) is a LT measurement.)

The origin of the unusual orientation of the C_{60} overlayer on the Ag(2ML)/Pt(111) dislocation network can be investigated best in the case of 0.4 ML coverage, where extended C_{60} islands are observed in the middle of terraces without any contact to the step-edges. Therefore the orientation of the C_{60} lattice is not influenced by the step-edges. Figure 3a shows a 40 nm x 40 nm STM image of such a C_{60} island. The hexagonal C_{60} lattice is readily observed, and it can be seen that the C_{60} close-packed <10> direction is well aligned with the direction of the dislocation lines, from which the alignment of the C_{60}<10> direction and the Ag<1-10> direction can be deduced. It can further be observed that the structure of the hcp1 domains and the neighboring deep dislocation lines are imprinted on this C_{60} island via triangular features. Figure 3b displays a line profile of the corrugation of the C_{60} overlayer. If one considers the tops of the C_{60} molecules, the corrugation is of the order of 35 pm, which is very close to that of the underlying dislocation network. Each triangular feature associated with a hcp1 domain consists of 10 C_{60} molecules, 1 central and 9 peripheral ones. The central molecule is imaged 15-20 pm higher than the 9 peripheral ones. This height difference is comparable to the Ag(2ML)/Pt(111) corrugation of 25 pm around the hcp1 domains (Figure 1b). It is evident that the central molecules occupy the centre of the hcp1 domains, and that the peripheral molecules are located at the deep dislocations of the Ag(2ML)/Pt(111) strain-relief pattern. We propose that it is this "locking" of the C_{60} molecules into the deep dislocations which determines the orientation of the C_{60} overlayer lattice on Ag(2ML)/Pt(111).
The inset of Figure 3a shows a C₆₀ island in a region where only a pseudomorphic 1 ML Ag is grown without the formation of any dislocation network. Here, the C₆₀ island adopts the usual (2\sqrt{3} \times 2\sqrt{3}) R30° orientation. If we assume that the deep dislocation lines of the Ag(2ML)/Pt(111) pattern represent the energetically most favorable adsorption sites, a C₆₀ lattice with the close-packed rows C₆₀<10> aligned along the deep dislocation lines is not unexpected. From a geometrical point of view, these favorable adsorption sites can be filled more efficiently if the C₆₀ lattice aligns the <10> rows with the dislocation lines. This filling of the deep dislocations would be much less effective for the usual (2\sqrt{3} \times 2\sqrt{3}) R30° orientation, where the non-close-packed <11> rows would be aligned with the dislocation lines. Although one unit cell of the dislocation network contains about 50 C₆₀ molecules and only 9 of those lock into the deep dislocations, the gain in absorption energy is apparently sufficient to rotate the whole lattice out of the usual (2\sqrt{3} \times 2\sqrt{3}) R30° orientation. This gain in adsorption energy is also corroborated by the observation of a compression of the C₆₀ lattice depending on the lattice parameter of the dislocation network. From Figure 3a we deduce a C₆₀ lattice constant of 9.3 Å, which is 7 % lower than the lattice constant of 10.0 Å in the C₆₀ bulk structure. An even higher compression of 20 % has previously been reported for a C₆₀ film on a reconstructed Au(001) surface [15].

Figure 3. (a) Topographic LT-STM image (40 nm x 40 nm, -2 V, 0.01 nA) from 0.4 ML C₆₀ coverage, displaying a 2D island with triangular features grown in the middle of a Ag(2ML)/Pt(111) terrace. A dual tone color scale has been chosen for this image to allow the visualization of both the C₆₀ lattice and the dislocation network of the substrate. For comparison, the inset shows a LT-STM image (20 nm x 20 nm, -2.5 V, 1.5 nA) of a C₆₀ island nucleated on a pseudomorphic Ag monolayer on Pt(111) (without any dislocation network), giving rise to the usual (2\sqrt{3} \times 2\sqrt{3}) R30° structure observed on the bare Ag(111) substrate [9-12]).

The origin of the gain in adsorption energy at the deep dislocation lines is not clear at this stage. More detailed investigations are needed and are currently being undertaken to fully understand the C₆₀ adsorption behavior on this complex template surface. First, a more detailed picture of the atomic structure of the Ag(2ML)/Pt(111) dislocation network is required. Second, C₆₀ adsorption at LT (77-150 K) and at low coverages is necessary to identify the energetically most favorable adsorption sites. Furthermore, scanning tunneling spectroscopy might allow to resolve spatial differences in the electronic structure of the dislocation network, which might contribute to the site specific molecule adsorption.
4. Summary
In summary, the formation of C$_{60}$ overlayers on the Ag(2ML)/Pt(111) strain-relief patterns has been studied by means of STM. Template surfaces exhibiting regular dislocation networks have been successfully prepared. At low sub-monolayer coverages, the C$_{60}$ molecules are mobile enough to diffuse across the dislocation lines and to decorate the step-edges. Increasing the C$_{60}$ coverage to around 1 ML shows that molecules grow layer-by-layer. At 0.4 ML C$_{60}$ coverage, hexagonally close-packed 2D islands are nucleated both at the step-edges and in the middle of terraces, without any contact to step-edges. These isolated C$_{60}$ islands show an unusual orientation of the hexagonal lattice as compared to C$_{60}$ islands on the bare Ag(111) substrate. Instead of a (2√3 × 2√3) R30° orientation as observed on the bare Ag(111) substrate, the C$_{60}$ lattice on Ag(2ML)/Pt(111) is rotated by 30° in order to align the close-packed C$_{60}$ rows with the dislocation lines running along the Ag <1-10> directions. This rotation of the molecular lattice appears to be driven by the locking of C$_{60}$ molecules into the deep dislocations surrounding the hcp1 stacking domains. The corresponding gain in adsorption energy seems to be significant since an ensuing compression of the C$_{60}$ lattice up to 7% can be observed.

Acknowledgements
We acknowledge financial support by the European Commission (RADSAS, NMP3-CT-2004-001561).

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