Multitude of PTCDA Superstructures on Ag(111) and Vicinal Surfaces

Supplementary Information

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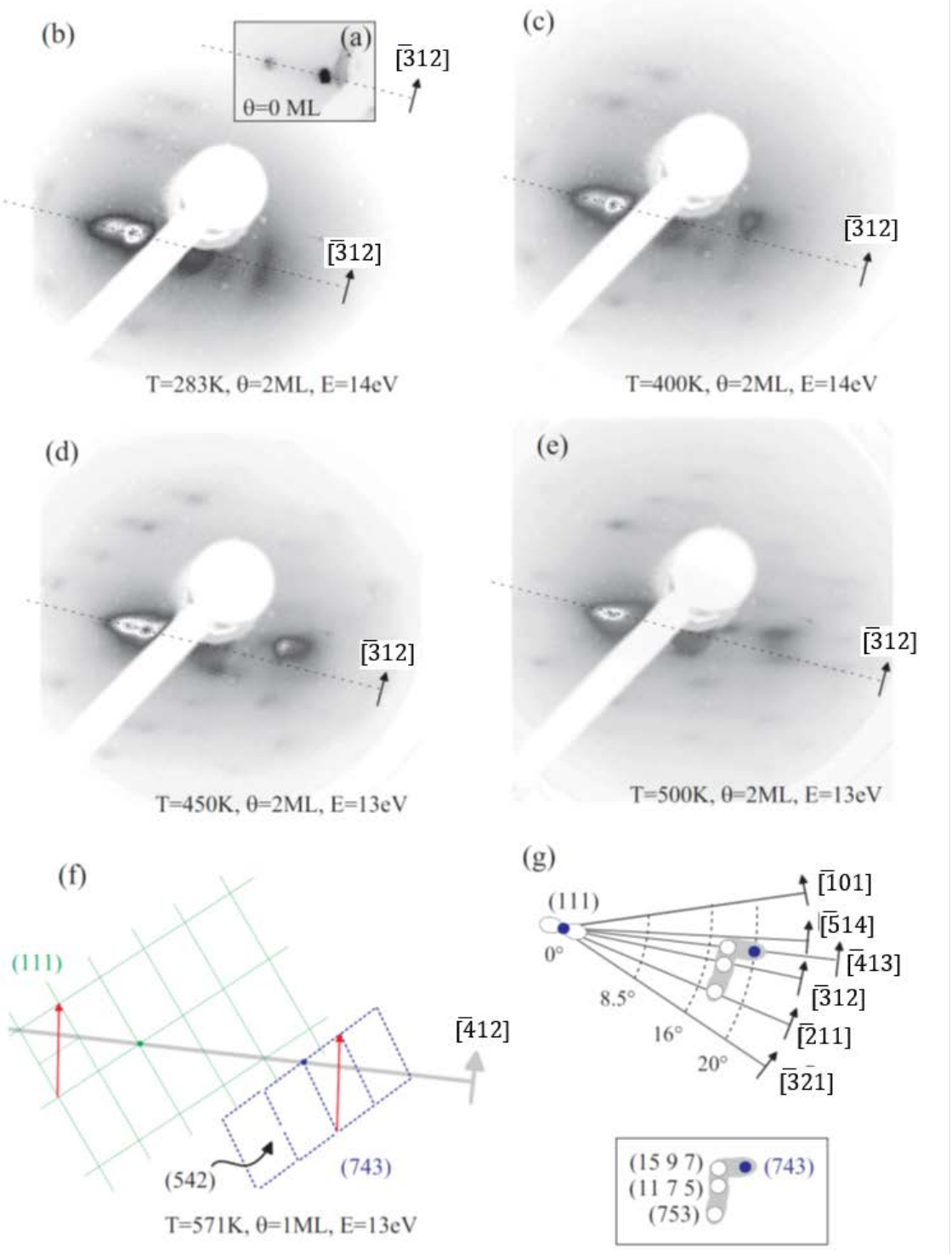
Fig. S1: LEED-Data demonstrating the formation of the (743)-facet on Ag(10 8 7) by annealing of a PTCDA bilayer stepwise up to 550 K after deposition at room temperature. The final (743)-facet is formed via several metastable facets with smaller inclination angle and is influenced by the $S_A(111)$ superstructure. Directions refer to real space (see (g)). This series indicates both, the amount of valuable information contained in such LEED images and the difficulty of extracting this information. The latter is due to the fact that i) the adsorbate domains are relatively small and hence the LEED spots are broad, ii) there are several different faces and superstructures contained in one LEED picture, iii) the spots move as function of energy, and iv) the spots may be split due to antiphase interference conditions on stepped (vicinal) surfaces.

S1a) shows the splitting of the (00) spot from a clean Ag(10 8 7) surface in antiphase condition. The fact that the two spots are relatively sharp as well as their behavior as function of energy (not shown) indicate that the surface consists of (111) terraces separated by mono-atomic steps with very regular distance.

S1b) – S1e) represent the surface changes after deposition of 2 ML PTCDA at room temperature and after stepwise annealing at the temperatures given. The splitting of the (00) reflection is reduced by a factor 2 indicating a preferential bunching of two steps and



a doubling of the widths of the (111) terraces to about 3.2 nm. Since PTCDA adsorbs on these terraces in the common $S_A(111)$ superstructure the corresponding superstructure spots are observed for only one domain (!). Moreover, weak (00) reflections from different, newly formed vicinal faces are found which have an inclination angle of 17.5°±0.5° and are distributed over a relatively large range of azimuthal angles. Upon annealing this range of reflections (containing facets like (15 9 7), (11 7 5), and (753); see S1g) is narrowed to one reflection which becomes dominant after annealing at 570 K and has moved to an inclination angle of 20.1°±0.5°; it represents the new (741) facet.

S1f) Result after annealing at 570 K. Now the bilayer has been desorbed, and the monolayer shows relatively sharp spots which can be summarized as follows: a fully developed single domain of an $S_A(111)$ structure on (111) terraces (green lattice in reciprocal space); (743) facets with strong (00) reflection and corresponding superstructure (blue lattice); (542) facets with weak (00) reflection (superstructure not discernible in this case). The latter facets are needed to keep the global orientation of the sample. Note that the diagonals of both superstructures are equal (red arrows) and run exactly along the [-413] step direction, i.e. the superstructure domain boundaries are commensurate along this direction.

S1g) Stereographic projection of the observed facets together with polar angles and step orientations.

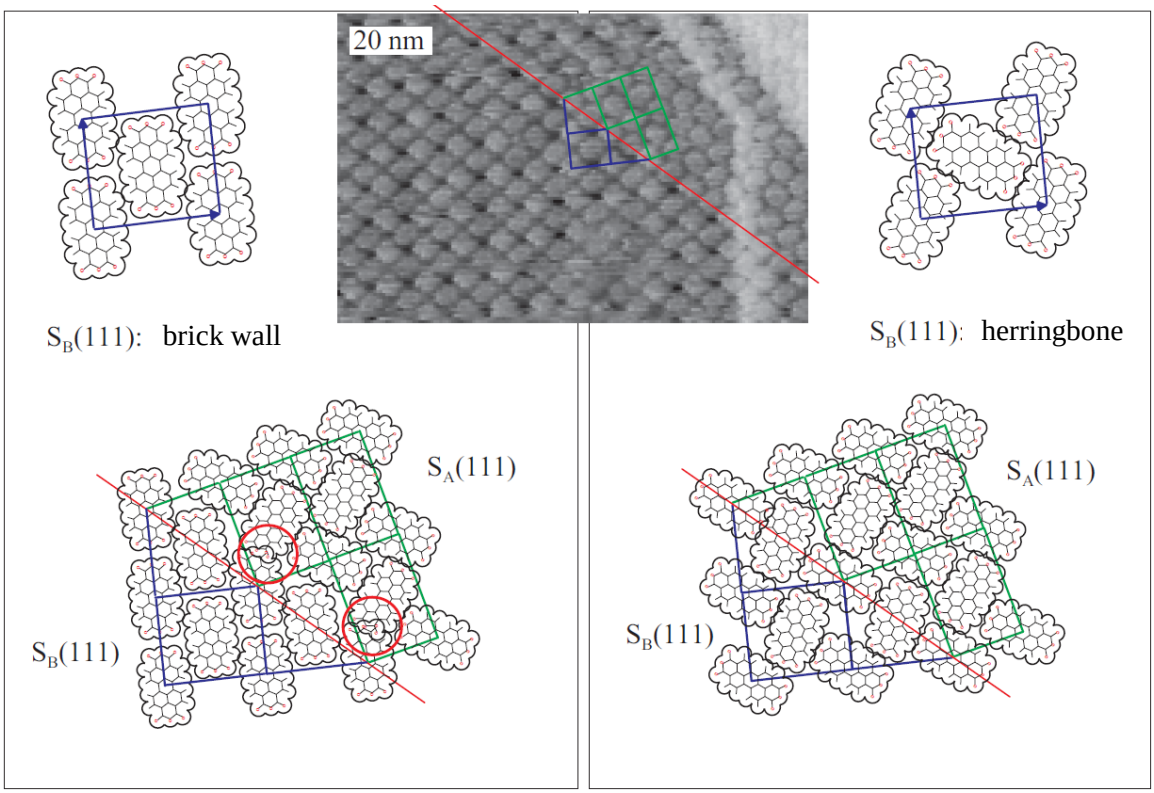


Fig. S2: Comparison of two different models for the orientation of PTCDA molecules within the unit cell of the $S_B(111)$ structure: herringbone vs brick wall structure. The adjacent $S_A(111)$ structure is of course identical. Note that the size of the unit cells, their orientations, and the distances along the red (border) line are given by the experiment while the positions of the PTCDA molecules within the $S_B(111)$ structure are suggestions. The significant overlap of molecules in the case of the brick wall structure is a strong argument against this suggestion.

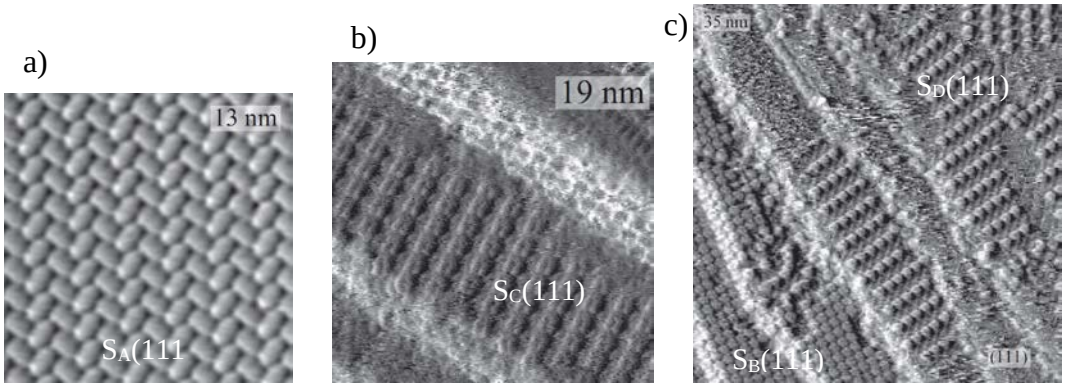


Fig. S3 a) STM image of $S_A(111)$ superstructure, which is the dominating structure on large (111)-terraces (FoV 13 nm). b) STM image of $S_C(111)$ superstructure, obtained by annealing of a PTCDA multilayer sample at 550 K or – as in the present case – by the influence of the STM tip (3 nA instead of 1 nA; 2 V) while scanning a $S_A(111)$ sample at room temperature (FoV 19 nm). c) STM image of $S_D(111)$ superstructure obtained after PTCDA deposition at 550 K on Ag(775); this structure preferentially occurs on large (111)-terraces at a coverage close to 1 ML. Four $S_D(111)$ domains and a neighboring $S_B(111)$ domain (bottom left) are displayed here.