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Long range orientation of meta-stable atomic hydrogen adsorbate clusters on the graphite(0001) surface

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Abstract

We present scanning tunneling microscopy (STM) images of meta-stable hydrogen adsorbate structures on the highly oriented pyrolytic graphite (HOPG) (0001) surface and identify two unique and stable hydrogen structures. One of these is observed after thermal anneals to 525 K at both high and low hydrogen coverage and is identified as a hydrogen dimer structure. The other, a novel, more complex structure not previously observed, appears only after thermal anneals at high hydrogen coverage and is observed to exhibit long range orientation within each micro-crystallite region on the HOPG surface.

1. Introduction

Adsorption structures of hydrogen atoms on graphite surfaces have attracted considerable interest during recent years due to their relevance within fields as diverse as interstellar chemistry, hydrogen storage, and plasma/fusion physics. In the area of interstellar chemistry molecular hydrogen formation from H atoms chemisorbed on graphite serves as a model system for H_2 formation in diffuse interstellar clouds, post shock regions and photo dissociation regions. In these regions hydrogen molecules are believed to be formed on the surface of bare dust grains [1], a substantial fraction of which are expected to be carbonaceous [2]. In connection with hydrogen storage, H chemisorbed on graphite is a model system for studying storage of hydrogen in atomic form, which opens up for the possibility of larger energy gains pr. stored H atom than what is obtainable with hydrogen stored in molecular form [3]. Finally within the area of fusion plasma physics the H graphite interaction plays an important role in the design of new Tokamac wall materials [4].

The chemisorbed state of atomic hydrogen on graphite was initially observed using ultraviolet photoemission spectroscopy [5]. Calculations show that such a chemisorbed state of a hydrogen atom above a carbon atom exist with a binding energy of 0.67 eV if the carbon lattice is allowed to relax such that the carbon atom above which the hydrogen atom is adsorbed puckers out of the surface by 0.3 Å. Due to the puckering a barrier of 0.2 eV exist to enter into the chemisorbed state [6,7]. Low energy electron diffraction (LEED) experiments show that hydrogen atoms do not adsorb in ordered structures on the graphite surface [8]. Hydrogen dimer structures have been directly observed and identified on low coverage graphite surfaces in scanning tunneling microscopy (STM) measurements [9,10]. Since the diffusion barrier for isolated H atoms chemisorbed on the graphite surface is larger than the desorption barrier and since density functional theory (DFT) calculations show reduced and in some cases even vanishing atom sticking barriers in the vicinity of already adsorbed H atoms the formation of these dimer structures is believed to occur via preferential sticking directly into dimer configurations [11,12]. Based on the STM studies two dimer structures are inferred to be most abundant on the graphite

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surface, namely the ortho-dimer structure where two hydrogen atoms are adsorbed on nearest neighbor carbon atoms and the para-dimer structure where two H atoms are adsorbed on opposite sides of a carbon hexagon. The existence of hydrogen quartet structures has also been proposed [13]. Atomic recombination to molecular hydrogen from chemisorbed atomic hydrogen on graphite has been observed via Eley–Rideal processes [14] and in temperature programmed desorption (TPD) measurements [15]. The TPD experiments showed evidence of a complex recombination mechanism with 1st order desorption kinetics and multiple desorption peaks. Combined STM and DFT studies have shown that at low coverage molecular hydrogen forms from recombination of H atoms which are prepaired in the para-dimer structure [9,11]. The ortho-dimer structure, on the other hand, is stable towards direct recombination and can only recombine via diffusion over the para-dimer configuration. This results in increased stability of the ortho-dimer structure causing a high temperature peak in the TPD spectra. Here, we present new STM results which reveal that at higher coverage a new, complex, meta-stable hydrogen structure exist which is as stable as the ortho-dimer structure and co-exist with this structure at temperatures up to 600 K.

2. Experimental methods

All experiments were performed using the home built Aarhus STM [16] under ultra high vacuum (UHV) at a base pressure below 3×10^{-10} Torr. A tungsten (W) STM tip was prepared via voltage pulse modification or high voltage treatment. HOPG samples were cleaved in air immediately prior to being inserted into the UHV chamber. In vacuum the samples were annealed to 1300 K by electron bombardment of the sample backside. Atomic hydrogen deposition was performed using a hot (1600–2200 K) hydrogen atom beam source (Either HABS 40 from MBE Komponenten or a similar Jülich type source [17]). The employed D atom flux was $\sim 10^{14}$ atoms cm^{-2} s^{-1}. The surface was kept at room temperature during deposition. The adsorption of hydrogen on the HOPG surface was confirmed by TPD experiments into a differentially pumped quadrupole mass spectrometer, equipped with a Fuelner cap cone with a 3 mm opening, which can be moved to within 1 mm of the sample surface. In the majority of the experiments, deuterium atoms were used to obtain a better signal to background ratio in the TPD experiments. All temperature measurements during sample treatment were performed by a type K thermocouple mounted on the backside of the HOPG sample. All STM images were recorded at room temperature.

3. Experimental results

Fig. 1a shows an STM image of a highly oriented pyrolytic graphite (HOPG) surface after a 12 min D atom deposition. The bright protrusions in the images are ascribed to clusters of chemisorbed D atoms since they only appear after D atom deposition and since they are correlated with molecular deuterium desorption measured in TPD. Fig. 1b displays an STM image after a 12 min D atom deposition as in Fig. 1a, followed by a thermal anneal to 525 K. Again, the bright protrusions in the images are ascribed to clusters of chemisorbed D atoms. Two different types of structures are visible in the image. One type is elongated ellipsoidal shapes with three different orientations while the other structure has a star like shape. Fig. 1c displays the statistical analysis of a larger series of STM images obtained by annealing the D covered HOPG surface depicted in Fig. 1a to subsequently higher temperature. Following 12 min D atom deposition at room temperature the surface was annealed to temperatures ranging from 500 to 570 K and the fraction of elongated ellipsoids and star structures was recorded as a percentage of the total number of D atom clusters on the surface. We find that as the annealing temperature increases, the total coverage decreases and the relative percentage of elongated ellipsoids and star structures is observed to increase until they become completely dominant. This indicates that the elongated ellipsoid and star structures are more stable than other hydrogen adsorbate structures observed on the graphite surface. The star and elongated ellipsoid structures are desorbed at temperatures above 550 K, coinciding with the high temperature D_2 peak observed in TPD experiments from atomic recombination of chemisorbed D atoms on graphite [15].

As discussed above a hydrogen dimer structure (the ortho-dimer) with high stability towards thermal anneals has previously been identified in STM experiments obtained following anneals of graphite surfaces with a lower coverage of D atoms [9]. This ortho-dimer state exhibited the same electronic characteristics and desorption kinetics as the elongated ellipsoids imaged by STM following anneal of the high-coverage surface displayed in Fig. 1a. We therefore identify the elongated ellipsoids in Fig. 1b as hydrogen ortho-dimers. The star-like structures in Fig. 1b has not been observed previously and are only observed following high D exposures.

Fig. 2 shows a series of STM images of a star like structure like the ones shown in Fig. 1a recorded at different scanning voltages. At high voltage, when the tip is far from the surface, the imaged structure is star like, while at low voltage, when the tip is close to the surface the structure appears as a triangle.

In Fig. 3a is shown a high-resolution zoom in on a star-like structure. D atoms chemisorbed on the graphite surface give rise to a large perturbation of the local electronic density of states at the adsorption site and also give rise to long range electronic modifications in the form of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ superlattice at distances as far away as 35 Å from the adsorption site [18,9]. At the edges of the image the undisturbed carbon lattice is observed. STM only images every second carbon atom on the graphite surface and the consensus is that the imaged atoms are carbon

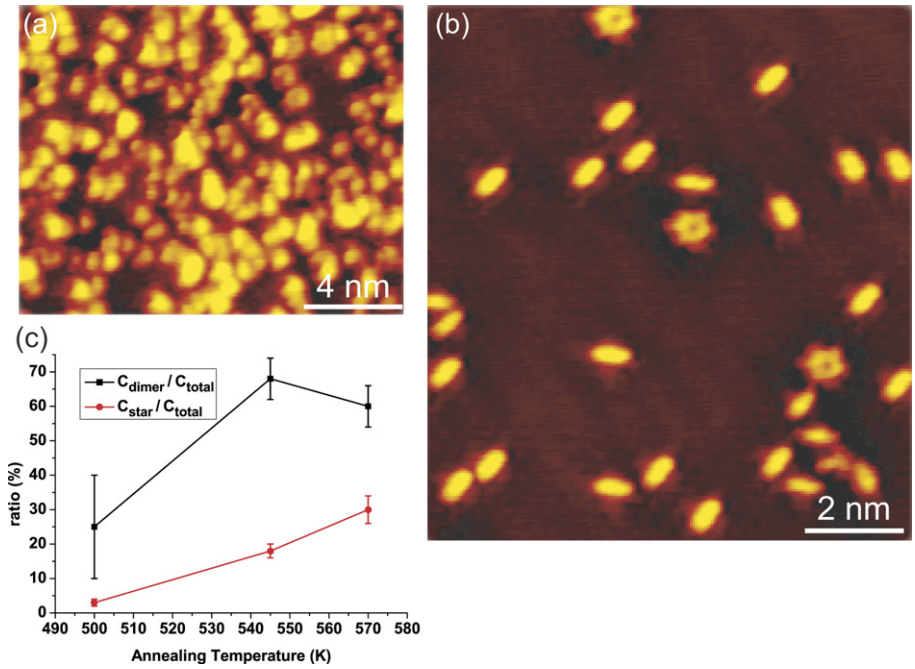

Fig. 1. (a) STM image of the graphite surface after a 12 min D atom dose. Imaging parameters: $I_t = -0.20$ nA, $V_t = -743$ mV. (b) STM image of the graphite surface obtained after a 12 min D atom dose followed by an anneal to 525 K. Imaging parameters: $I_t = -0.18$ nA, $V_t = -1051$ mV. (c) The relative percentage of star and dimer clusters as a function of annealing temperature. Data were obtained following anneals to 500 K, 545 K and 570 K.

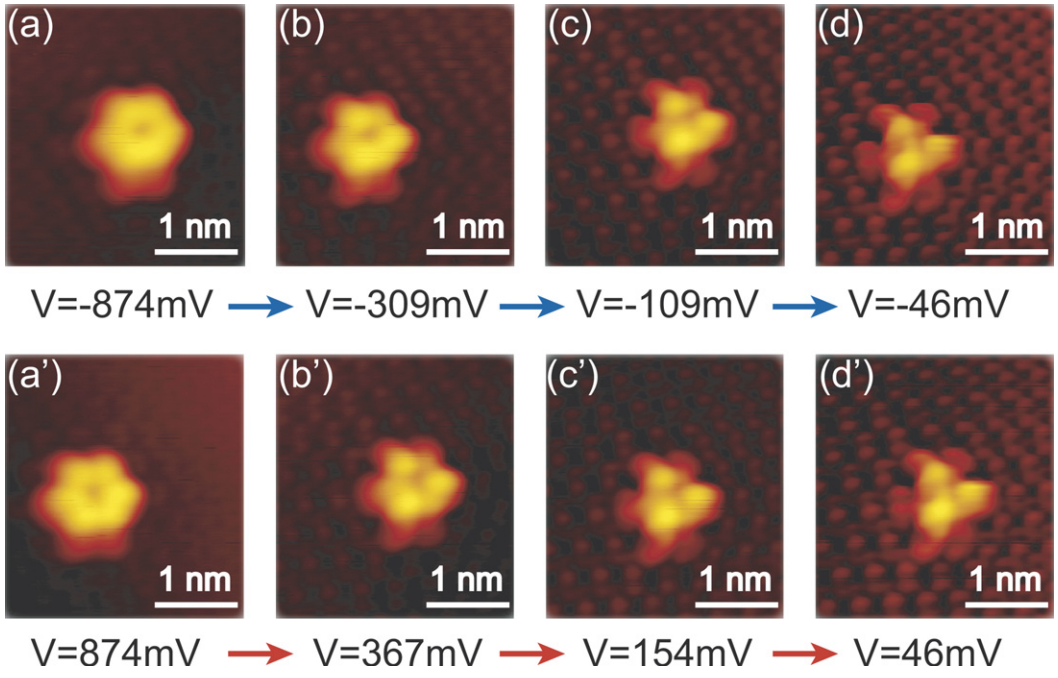

Fig. 2. Star-structure imaged at varied bias voltage, $I_t = \pm 0.15$ nA. At low bias voltage, i.e. when the STM tip is in close proximity to the surface, the star-structure appears triangular in the STM images.

atoms in β sites [19], i.e. carbon atoms with no neighbor in the underlying carbon layer vs. α atoms that do have a neighbor in the underlying layer. In Fig. 3a a graphite lattice has been overlaid on top of the high-resolution STM image. The positions of the β carbon atoms is represented by big dots. The star structure in the image is observed to be centered on a β carbon atom. The position of the α carbon atoms cannot be unequivocally determined based on the STM image, since two possible mirror-images of the graphite lattice exist, with interchanged α carbon atom and hollow site positions, which give rise to the imaged carbon atom structures in Fig. 3a. One of the two possible graphite lattices is superimposed on the image with the small dots representing one of the two possible positions

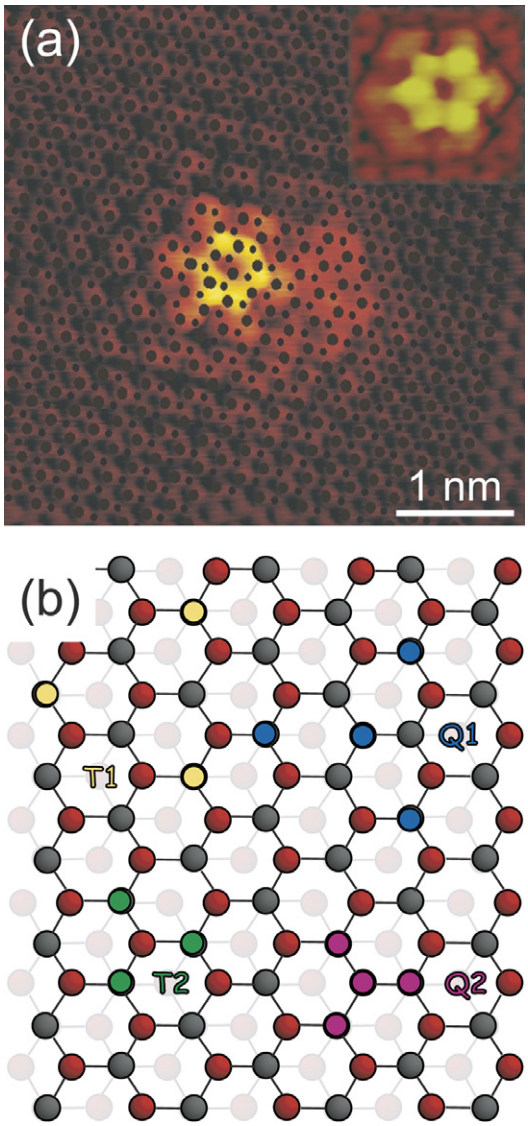

Fig. 3. (a) STM image of a star-like structure with superimposed model graphite lattice. Imaging parameters: $I_t = -0.53$ nA, $V_t = -1051$ mV. The bright shape to the right of the star structure is ascribed to imperfections of the tip. The inset shows a star-like structure imaged without tip induced asymmetry. Imaging parameters: $I_t = -0.79$ nA, $V_t = -743$ mV. (b) 3 and 4H atom structures exhibiting the same symmetry as the observed star-like structure. H atom positions marked as: trimer structure: T1: yellow dots, T2: green dots, Quartets: Q1: blue dots, Q2: purple dots, α carbon atom are grey dots, while β carbon atoms are red. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

of the α carbon atoms. For either of the two possible graphite lattices, three of the bright bumps in the star-like structure are on top of α-atom positions, while three are in the hollow sites of the honeycomb lattice. The bright shape to the right of the star structure is ascribed to imperfections of the tip. The inset in Fig. 3a shows a star-like structure imaged without tip induced asymmetry. Three very bright and three slightly darker protrusions can be identified.

In Fig. 3b a number of possible 3 and 4 H atom candidate structures for the underlying H atom configuration responsible for the star-like structure are shown. These are all centered on a β carbon atom and exhibit the same C_3 symmetry as the star-triangle-like feature in the STM images.

Fig. 4a–c shows a series of STM images where the star-like structure is imaged at low voltage resulting in a triangular appearance. As can be seen from the images all the triangles within a given image are oriented in the same direction. Observations show that generally all triangles within a given area (micro-crystallite) of the HOPG surface are oriented in the same direction. Such an aligned orientation is rather surprising considering that the star structures are observed to be centered on a carbon atom. In Fig. 4d it is sketched how for any structure with the same symmetry as the observed star structure centered on a carbon atom another one must exist pointing in the opposite orientation (rotated 60°), the only difference with respect to the original being whether it is centered on a β or an α carbon atom. Thus our observation that all the triangle-structures point in the same direction is equivalent to the fact that all of them are centered on beta atoms which seems to imply a significant energy difference between similar structures centered on alpha and beta atoms. This observation is in contradiction to previous theoretical results according to which the adsorption energy for individual H-adatoms is only weakly dependent on the type of surface carbon atom onto which it is adsorbed [7]. However, calculated binding energy differences between hydrogen atoms on α and β sites of 10% have been reported in one instance [20]. One alternative explanation might be that the structures contains sub-surface hydrogen atoms. A larger binding energy difference between α and β sites is expected if the hydrogen atom is adsorbed sub-surface [21]. However, large barriers exist for an incoming hydrogen atom to go sub-surface and be intercalated between the graphite layers [22] making this explanation dubious. Previous studies of H atom dimer structures on graphite have shown that it is not the binding energies but rather the kinetics of the sticking, diffusion and recombination processes which determine what structures are formed and how stable these structures are [9,11]. Whether a more subtle difference between the α and β sites exist in the hydrogen adsorbate structure formation dynamics or in the kinetics of the hydrogen atom recombination and desorption remains unclear. It has also been suggested that the star-triangle-like structure could be a result of a hydrogen induced defect [23]. Finally, an alternative explanation could be that the observed long range disturbance which the hydrogen adsorbates causes in the electronic density of states of the carbon lattice results in a real or apparent alignment of the star-triangle-like structures within a given area.

In conclusion, we have observed that hydrogen atoms at high coverage forms two types of meta-stable structures with increased stability, namely dimer like structures, which were also observed at low coverage, and star/triangular-like structures, which are unique for the high coverage regime. These structures are stable against anneals up

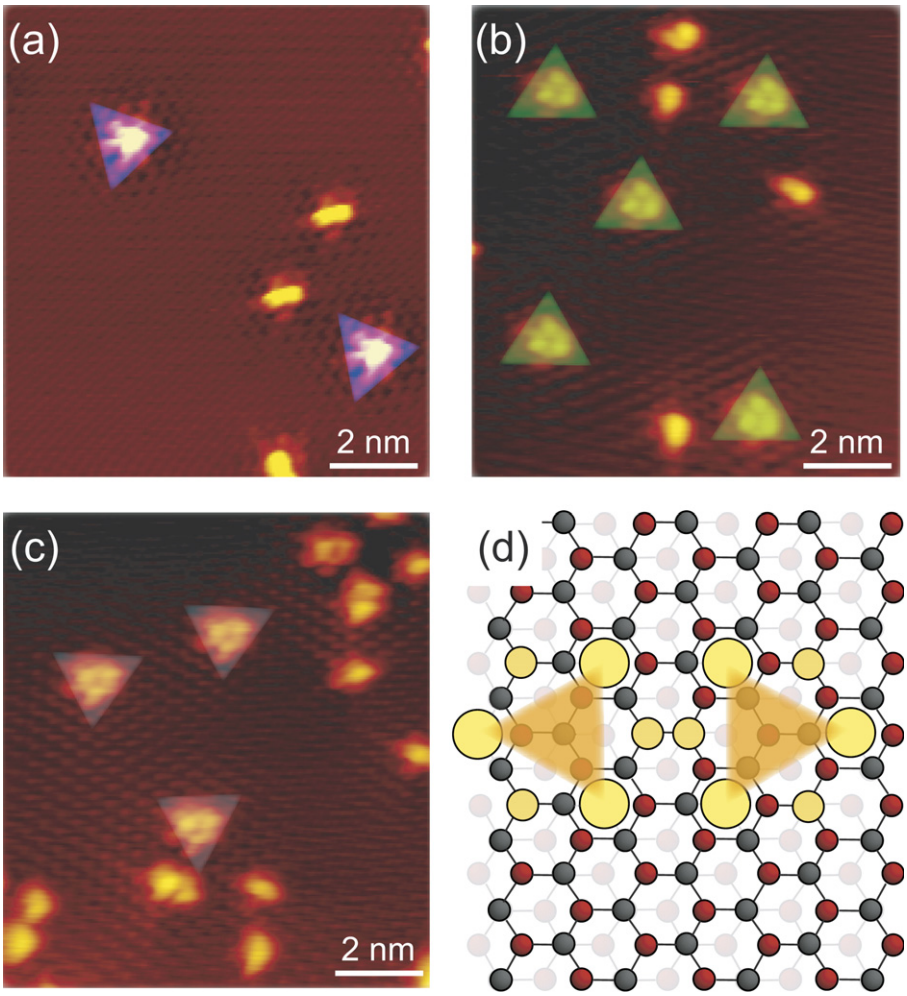

Fig. 4. (a)–(c) STM images of different regions (different micro-crystallites) on the graphite surface recorded in an imaging mode where the star-structures appear triangular. All star structures, e.g. all the triangles, in a given region are seen to have the same orientation. For clarification highlighted triangles have been superimposed. Imaging parameters: (a) $I_t = -0.49$ nA, $V_t = -1051$ mV, (b) $I_t = -0.19$ nA, $V_t = -743$ mV, (c) $I_t = -0.14$ nA, $V_t = -743$ mV. (d) Schematic drawing of the two orientations expected for a triangular structure centered on either an α (grey) or a β (red) carbon atom. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

to 525 K and are expected to be responsible for the high temperature peak observed in TPD measurements of molecular hydrogen formation by atomic hydrogen recombination on the graphite surface. The star/triangular-like structures are observed to be centered on carbon atoms on the surface and are imaged either as stars or triangles depending on the imaging parameters. Imaged as triangles they are observed to exhibit the same orientation within a given micro-crystallite on the surface. The origin of this orientation and the exact hydrogen adsorbate structure which gives rise to the imaged star/triangular structure is not yet determined, thereby underlining the fact that we still do not fully understand the complex dynamics which underlie the H-graphite interaction.

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