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Hydrogen chemisorption on sp^2 -bonded carbon: Influence of the local curvature and local electronic effects

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ABSTRACT We report on the interaction of hydrogen with sp^2 -bonded carbon which has been investigated on graphite (0001), single-walled carbon nanotubes and C_{60} multilayer films. These substrates have been chosen to represent a large range of curvature in the carbon network. The photoelectron spectroscopy study of the samples treated with atomic hydrogen and low-energy hydrogen ions reveals that hydrogen is chemisorbed on the basal plane of the sp^2 -bonded carbon networks, as evidenced by the lowered emission from π -derived states and a lowering of the electron work function of up to 1.3 eV. The hydrogen adsorption energy barrier is found to strongly depend on the local curvature of the carbon network whereby the barrier is lowered with increasing curvatures. Whereas in the case of C_{60} and single-walled carbon nanotubes, hydrogen chemisorption can be achieved by exposure to atomic hydrogen, the chemisorption on graphite (0001) requires hydrogen ions of low kinetic energy (~ 1 eV). Furthermore, the adsorption energy barrier is found to increase with hydrogen coverage.

The scanning tunnelling microscopy study of individual adsorption sites on the graphite (0001) surface reveals long-ranged (~ 5 nm) electronic effects observed as a $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure in the local density of states. It is shown that this superstructure is due to the scattering of delocalized electron wavefunctions at the point defects. The resulting standing waves induce a redistribution of the local density of states which is directly related to the point-like Fermi surface of graphite.

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to act as strong scatterer for the delocalized electrons. Scanning tunnelling microscopy (STM) allows the direct characterization of the electronic effects of single point defects and reveals a typical range of the electronic effects of the order of 5 nm for single point defects [4–6]. Similar long-range effects have been observed in low-temperature measurements on metal surfaces where they are known as Friedel oscillations [7–9].

Additional interest in the interaction of hydrogen with sp^2 -bonded carbon stems from the possibility that interstellar dust particles containing graphite play a catalytic role for the H_2 formation from atomic hydrogen in interstellar space. In this context, several theoretical investigations have been conducted in order to determine the interaction potential between hydrogen and graphite including different relaxation possibilities of the graphite lattice [10, 11].

The chemical binding of hydrogen to an sp^2 -bonded carbon network requires a local rehybridization from sp^2 to sp^3 and has therefore a rather large adsorption energy barrier for a strictly planar sp^2 -bonded carbon network. This barrier is expected to be modified if the sp^2 -bonded network follows a curved surface. In order to study the effect of curvature on the adsorption properties of hydrogen, we chose three types of closed sp^2 -bonded carbon structures, namely graphite (0001), single-walled carbon nanotubes (SWNT), and C_{60} , covering a large range of possible curvatures.

In the second part of the paper we present STM results on the electronic structure of single point defects, namely hydrogen adsorption sites and atomic vacancies, on the graphite surface and discuss the scattering behavior of defects in relation to the observed redistribution of the local density of states (LDOS).

1 Introduction

Defects are known to play an important role in the local modification of electronic properties of solids. Their role as electron scatterers and creators of tunnelling junctions has recently been evidenced on carbon nanostructures and has even allowed the realization of single molecular electronic devices [1–3]. Chemisorption of hydrogen on sp^2 -bonded carbon is an interesting candidate for the local modification of the electronic properties since it leads to a local rehybridization from sp^2 to sp^3 of the carbon network. As a consequence, the π -states are locally removed which is expected

2 Experimental

Sample treatment and characterization were conducted in a photoelectron spectrometer (Omicron) modified for sequential angle-scanning data acquisition having a room temperature AFM/STM connected to the chamber. The spectrometer is equipped with a twin-anode X-ray source (Mg K_{α} , Al K_{α}) for X-ray photoelectron spectroscopy (XPS), and a He discharge lamp for ultraviolet photoelectron spectroscopy (UPS), and has been extended with an electron cyclotron resonance (ECR) microwave plasma source and an atomic hydrogen source.

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Typical plasma treatments were conducted at a hydrogen pressure of 10^{-2} mbar which results in an ion energy distribution with most of the ions having a kinetic energy around ~ 1 eV and a maximum detected energy of ~ 16 eV [12]. In order to be able to distinguish between hydrogenation due to hydrogen ions and atomic hydrogen, which are both present in the hydrogen plasma, an atomic hydrogen source was used with the design proposed by Bischler et al. [15], where the hydrogen molecules are dissociated in a heated tungsten tube (1700°C), through which the hydrogen is dosed onto the sample at a background pressure of 3×10^{-8} mbar.

Atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) measurements were performed in the combined mode of AFM/STM, using the normal force as a feedback signal and applying a fixed bias voltage between the sample and the tip. The recording of the piezo z -position and the tunnelling current allows the simultaneous determination of the topography and the LDOS. For this measurement mode we used AFM tips coated with highly conductive boron doped CVD-diamond.

3 Influence of local substrate curvature

We investigated the interaction of hydrogen with sp^2 bonded carbon as a function of the local curvature of the graphitic network. Adsorption experiments on graphite (0001), SWNT, and C_{60} multilayer films cover a local radius of curvature of the sp^2 -bonded carbon network ranging from $r = \infty$ for graphite to $r = 3.55 \text{ \AA}$ for C_{60} .

3.1 Graphite

Figure 1 shows UV (He I, $h\nu = 21.2 \text{ eV}$) photoemission spectra of the C(0001) surface taken for different polar emission angles ϑ along the Γ - K direction of the Brillouin zone. The angle-resolved measurements allow a clear attribution of the photoelectron features to the various valence bands of graphite. Spectra in the Γ - K direction are dominated by two prominent dispersing features, which are due to emission from a σ -band, dispersing from $\sim 9.5 \text{ eV}$ binding energy at $k_{\parallel} = 1.2 \text{ \AA}^{-1}$ to lower binding energies towards the Γ point, and emission from a π -band dispersing from the Fermi level at $k_{\parallel} = 1.70 \text{ \AA}^{-1}$ to $\sim 8.5 \text{ eV}$ binding energy at the Γ point. The low-energy cut-off of the valence band spectrum reveals a work function of 4.5 eV for the untreated sample.

Exposing the sample to atomic hydrogen does not affect either the work function nor the relative intensity of π - and

σ -features. This indicates that the energy of atomic hydrogen is not sufficient to overcome the adsorption energy barrier for hydrogen chemisorption on the flat graphite surface.

The situation is different when the C(0001) surface is treated with H_2 plasma. Doses of $\sim 10^{14}$ ions/ cm^2 induce modifications in the electronic structure. The intensity of features related to the π -bands decrease as a function of the plasma treatment time, showing that the hydrogen ions are sufficiently energetic to chemically bind to carbon atoms of the basal plane of graphite. Analysis of individual spectra shows, that the ratio between the intensities of π - and σ -states drops by a factor of ~ 1.7 for the longest treatment time (320 s) [12]. At the same time, secondary-electron emission at low kinetic energies is enhanced by a factor of ~ 2 and a non-dispersing feature at $\sim 10 \text{ eV}$ binding energy appears with increasing coverage of chemisorbed hydrogen. This feature is consistent with the hydrogen-related state found in density-of-states calculations for this C-H configuration [16].

Beside the changes observed on the π -derived states, distinct changes in the work function are observed upon hydrogen adsorption on the basal plane of graphite. Investigation of the low-energy cut-off of the valence band spectra reveal a maximum lowering of 0.4 eV of the electron work function [12]. The lowering of the work function indicates a change in the surface dipole, which is related to the adsorption of an element which has a different electronegativity than carbon. The observed shift to lower work functions is in agreement with hydrogen adsorption on top of the graphite layer since hydrogen has a lower electronegativity than carbon. A similar effect on the work function is observed for the hydrogen-terminated diamond surface [17].

3.2 Single-walled carbon nanotubes

Similar experiments as for graphite have been conducted on SWNT, which can be looked at as rolled up graphene sheets resulting in tubules with diameters of $d_T \geq 4 \text{ \AA}$ [18]. Valence band states with binding energies lower than $\sim 4 \text{ eV}$ are pure π -states and are expected to change in intensity upon hydrogen chemisorption on the tubes.

For the investigations on SWNT's we used buckypaper produced out of commercially available SWNT (Tubes@Rice, Carbon Nanotechnologies Inc.). Raman analysis of the radial breathing mode [19] revealed a mean tube diameter of $d_T \approx 1.2 \text{ nm}$.

FIGURE 1 Angle-resolved spectra in the Γ - K direction for the untreated C(0001) surface and after 180 s H_2 plasma treatment using He I (21.2 eV) radiation and an energy resolution of 60 meV . Spectra are taken for polar angles in the range between 62° and 20° with increments of 2° and are represented as a function of the parallel component of the photoelectron wave vector in a linear greyscale with black corresponding to maximum intensity

FIGURE 2 Valence band spectra of SWNT's for the untreated sample (circles), and for the saturation hydrogen coverages achieved with atomic hydrogen (triangles) and with hydrogen plasma (squares). The dotted line shows the gauss-background that has been subtracted for the intensity determination on the π -derived states. Adapted from [12]

In contrast to graphite, treatments with atomic hydrogen induce changes in the valence band of SWNT showing up as a reduction of the intensity on the pure π -state at 2.5 eV binding energy. For a treatment time of 120 s the intensity reduction on the π -derived states has achieved its saturation value of $\sim 22\%$ (Fig. 2) and the work function has been lowered by 0.3 eV to a value of 4.1 eV [12]. This indicates the conversion of delocalized π -states to C-H bond states with σ -character, which have a binding energy of ~ 10 eV [16, 20]. These new states are observed as increased emission from valence band features with ~ 10 eV binding energy. This indicates that a significant coverage of chemisorbed hydrogen can be achieved on the tube walls of SWNT by exposure to atomic hydrogen.

Further hydrogenation of the SWNT can be achieved by H_2 plasma treatment. This is exhibited as a further reduction of the intensity of the π -derived features down to $\sim 50\%$ of its original value, suggesting a hydrogen coverage of $\theta \simeq 0.5$. The change in work function amounts to -0.6 eV, indicating a significant change in the surface dipole. This lowered work function and electronegativity arguments suggest that on SWNT, hydrogen is chemisorbed preferably on the outside of the tube walls. Annealing of the sample to $\sim 800^\circ\text{C}$ restores the valence band structure and the work function of the untreated sample, indicating that all of the hydrogen has desorbed at this temperature.

3.3 C_{60}

Hydrogen adsorption experiments on C_{60} were performed on a multilayer film (~ 60 Å) grown on a Cu(111) single crystal. Exposing the film to atomic hydrogen reduces

FIGURE 3 Valence band spectra of the multilayer C_{60} film after different hydrogenation steps. From bottom to top: untreated multilayer film; hydrogen saturation coverage with atomic hydrogen; after 2 s of hydrogen plasma treatment; for hydrogen saturation coverage achieved with hydrogen plasma

the spectral weight of the pure π -derived molecular states (HOMO and HOMO-1, [21]) considerably (Fig. 3). For the saturation coverage achieved with atomic hydrogen, the relative intensity on the pure π -derived states is reduced to 53% and the work function is lowered by 0.8 eV, as compared to the untreated sample [12]. This indicates a hydrogen coverage of $\theta \simeq 0.5$ on the C_{60} molecules.

Further hydrogen adsorption can be achieved with hydrogen plasma treatment. Comparison of the valence band spectra of a film treated with atomic hydrogen (saturation coverage) and another film treated for 2 s in the hydrogen plasma shows that the evolution of the spectral features upon hydrogenation is identical for plasma and atomic hydrogen treatments. This further confirms that damage induced by hydrogen ions can be neglected at least for plasma treatments up to this level. The maximum reduction on the pure π -states is observed after a plasma treatment time of 115 s. This indicates a hydrogenation as high as $C_{60}H_{40}$ and is comparable to the hydrogenation that has been achieved via Birch reduction ($C_{60}H_{36}$, [22]). The work function of this film is lowered by 1.3 eV, as compared to the untreated sample.

3.4 Influence of local curvature

As described above, hydrogen adsorption depends very much on the chosen sp^2 -bonded carbon substrate. The important parameter that changes the adsorption energy barrier on the investigated carbon structures is the local curvature in the sp^2 -bonded carbon network. The introduction of curvature can also be looked at as a partial tetrahedrization

FIGURE 4 Work function change compared to the observed lowering on the π -state intensity on graphite, single-walled carbon nanotubes and C_{60} -molecules. Values are given for the saturation coverages of atomic hydrogen (H) and hydrogen plasma (H^+) treatments. The error on the determination of the relative intensity is estimated to be ± 0.1 and is mainly due to the error on the background subtraction

to the local bonding configuration leading to the admixture of sp^3 -character. This decreases the adsorption energy barrier for hydrogen chemisorption which requires a local rehybridization from sp^2 to sp^3 . This lowered energy barrier for strongly curved structures is evidenced by the fact, that atomic hydrogen can be adsorbed on C_{60} and SWNT, but not on graphite. Figure 4 summarizes the results for the saturation coverages achieved with atomic hydrogen and hydrogen plasma treatments on the investigated sp^2 -bonded carbon samples. The nearly linear behavior between the intensity on π -related features and the work function lowering indicates the dipole change induced by hydrogen chemisorption and shows, by electronegativity arguments, that hydrogen is mainly chemisorbed above the carbon layer.

Similar findings on the curvature dependence result from theoretical investigations [10, 11]. The results show that on-top adsorption is energetically favorable and that the energy barrier is considerably decreased when the carbon atom is raised to a more tetrahedral geometry. Figure 5 shows the calculated potential energy for an approaching hydrogen atom for two different geometries of the carbon network [11]. The energy barrier vanishes if the central carbon atom is protruded from the flat geometry (upper curve) to a more tetrahedral position ($h = 0.36 \text{ \AA}$). The curvature of the structures investigated in our work can be expressed by protrusions of the carbon atoms that are $h = 0$ for graphite, $h = 0.11 \text{ \AA}$ for SWNT and $h = 0.29 \text{ \AA}$ for C_{60} . Accordingly, one expects an adsorption energy barrier that is situated between the two curves shown in Fig. 5. However, the actual potential seen by the approaching hydrogen atoms depends on how fast and to which extent the carbon atoms can relax to energetically more favorable positions.

Beside the curvature, the hydrogen coverage also plays an important role for the adsorption energy barrier. This is seen in a limited coverage that can be achieved on C_{60} and SWNT

FIGURE 5 Interaction potential as a function of hydrogen-substrate distance as calculated by Sha et al. [11] for top site adsorption. The upper curve shows the result for flat geometry. The lower curve shows the potential for a protruded ($h = 0.36 \text{ \AA}$) carbon atom

with atomic hydrogen and the fact that further hydrogen adsorption can be achieved by exposure to a more energetic hydrogen species of a H_2 plasma.

Considering the theoretical works [10, 11], and our experimental results, suggests that the adsorption energy barrier is reduced for all hydrogen coverages when the local curvature in the sp^2 -bonded carbon network is increased [12].

4 Local electronic effects

Figure 6a shows an overview current image of a graphite surface after a short (3 s) hydrogen plasma treatment. The low defect density enables the investigation of the local structure of the defect, as well as the long-range electronic effects of individual defects. The combined mode of AFM/STM allows the distinction between two types of defects, namely hydrogen adsorption sites and atomic vacancies. Atomic vacancies are identified by local depressions in the topography signal, whereas hydrogen adsorption sites are not detected in the AFM signals [6]. Vacancy type defects appear with a density that is about four times lower than that of adsorption type defects, and are thought to be induced by the small part of higher energetic hydrogen ions present in the plasma.

The common feature of both types of defects is a long-ranged rearrangement of the LDOS, as observed in the simultaneously recorded current image. This rearrangement is characterized by a $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure with a range of the order of 5 nm, as determined for isolated defects.

The observed superstructure is related to scattering of the electronic states at point defects, which leads to the formation of standing waves in the vicinity of the defect. The structure of the related redistribution of the LDOS can be understood by examining the Fermi surface of graphite. The allowed states at the Fermi energy E_F are located at the corners, defined by the vectors k_j in Fig. 6, of the hexagonal Brillouin zone.

FIGURE 6 **a** Overview current image. The image has been recorded in AFM contact mode ($15 \text{ nm} \times 13 \text{ nm}$). Force setpoint: 2 nN; tunneling bias 50 mV. The current varies from 2 nA (black) to 35 nA (white). The defect on the right side shows local depressions in the AFM signal, whereas the defects on the left side are invisible for AFM signals. **b** Reciprocal lattice vectors and the 2D Brillouin zone (grey area) of graphite. The vectors $\mathbf{k}_j$ give the position of the K points. **c** Two-dimensional FFT of the current image shown in **a**. The spots forming the inner hexagon represent the $\sqrt{3}$ -superstructure observed in the vicinity of the defects. Spots forming the larger hexagon rotated by 30° appear as wave vectors that correspond to reciprocal lattice vectors $\mathbf{G}$. The outermost spots arise from the second harmonic of the inner hexagon. The spot at $\mathbf{k} = 0$ has been removed for better visibility of the relevant features

Backscattering at defects such as steps or point defects requires a momentum change of $-2\mathbf{k}_F$, $\mathbf{k}_F$ being the Fermi wave vector of the incoming electronic state. This large momentum scattering is also observed at metal surfaces leading to Friedel oscillations with a periodicity that is related to the Fermi wave vector of the surface states. Since in the case of metals, the involved charges form a free electron gas, there is no firm relation between $\mathbf{k}_F$ and the reciprocal lattice vectors and consequently, the related distribution in the LDOS is not commensurate with the underlying atomic lattice. On graphite, however, there is a relation between the lattice and the Fermi wave vectors, since they coincide with the corners of the first Brillouin zone. Therefore, the required momentum change is reduced to $\mathbf{q} = \mathbf{k}_F$ if an appropriate reciprocal lattice vector is taken into account (Fig. 6b). This explains the $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure where the corresponding spots in the Fast Fourier Transform (FFT) coincide with the corners of the Brillouin zone, i.e. with the Fermi wave vectors.

The similar long-range behavior of the defects indicates that both atomic vacancies and hydrogen adsorption sites are strong scatterers for the delocalized electron wavefunctions, which is related to the fact that in both cases, the π -states are locally suppressed.

5 Summary and conclusion

We have studied the interaction of atomic hydrogen and low energy hydrogen ions with sp^2 -bonded carbon surfaces of different local curvatures. Hydrogen chemisorption on the basal plane is evidenced by a reduction of the spectral weight of π -related features of the valence band, induced by the transformation to more tightly bound σ -derived C-H bond states. Furthermore, hydrogen chemisorption leads to a lowering of the electron work function of up to 1.3 eV (C_{60} multilayer film) which is attributed to a change in the surface dipole and, by electronegativity arguments, indicates hydrogen adsorption above the surface carbon layer.

The results show that the adsorption energy barrier depends on the local curvature in such a way that the barrier is lowered with increasing curvature. The behavior is attributed to the higher sp^3 -character of convex sp^2 carbon structures. In addition, the adsorption energy barrier increases with the hydrogen coverage as evidenced by different saturation coverages for treatments with atomic hydrogen and hydrogen ions.

The AFM/TM investigation of the hydrogen plasma treated graphite surface reveals two types of defects that could be assigned to hydrogen adsorption sites and atomic vacancies. Both defects induce long-ranged electronic effects that are observed as a $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure in a range of $\sim 5 \text{ nm}$. It has been shown that this superstructure reflects the standing waves formed by the backscattering of the delocalized electron wavefunctions from point defects.

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