Creation and STM/STS investigations of hydrogen ions induced defects on single-walled carbon nanotubes

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Abstract. We report on a technique able to create low-energy hydrogen ions induced defects on single walled carbon nanotubes (SWCNT) using a hydrogen electron cyclotron resonance (ECR) plasma source. Low temperature scanning tunneling microscopy (LT-STM) investigations revealed defect sites with hillocks-like features between 1 Å and 3 Å in height and lateral spreading between 0.5 nm and 2 nm. Scanning tunneling spectroscopy (STS) measurements on a metallic SWCNT revealed a strong modification of the electronic structure on a specific defect zone characterized by a pronounced peak in the local density of states (LDOS) close to the Fermi energy.

1. Introduction

Since their discovery in 1991 [1], carbon nanotubes have stimulated intensive research due to their outstanding physical properties. One special field of interest is the use of single walled carbon nanotubes (SWCNT) in electronic devices of nanometer dimensions. A SWCNT can be regarded as a single graphene sheet rolled up in such way to form a hollow cylinder with diameter of the order of one nanometer. The electronic properties of the SWCNT will depend on the way the graphene sheet has been rolled into the cylinder, which is expressed by the so-called chirality vector $\mathbf{C}$. The chirality vector can be expressed as linear combination of the two basis vectors ($\mathbf{a}_1, \mathbf{a}_2$) of the graphene lattice ($\mathbf{C}=n\mathbf{a}_1+m\mathbf{a}_2$), therefore a SWNT is usually characterized by the two integer components of $\mathbf{C}$, $n$ and $m$. Depending on the values for $n$ and $m$, which means on the chirality and the diameter, SWCNT can be either metallic or semiconducting [2,3]. Accordingly, during the last decade, SWCNT have proven their great potential as electronically active material in electronic devices such as field effect transistors (FET) [4,5] or single electron transistors (SET) [6-8]. It is clear that the implementation of SWCNT based electronic devices requires a deep understanding of the structural and electronic properties of SWNT. Using low-temperature electronic transport measurements and scanning tunneling spectroscopy (STS) a very good understanding of the intrinsic electronic properties of SWNT could be achieved. However, it was also found that the behaviour of real SWCNT devices is not only determined by the intrinsic electronic properties of the perfect SWNT but that local defects play a very important role. As an example it was demonstrated via scanning gate microscopy (SGM) that in SWNT-FET the transconductance is very sensitive on the location on the SWCNT where the gate voltage is applied. The highest transconductance is observed at defects in the SWCNT [9,10], where the exact nature of these defects could not be resolved. From these findings however it becomes...
clear that SWCNT-FET properties can be influenced and may be controlled by defects. Defects may also be important in the creation of quantum dots (QD) on SWCNT. The tunnel barriers defining a QD in experimentally realized SETs are generally created by the high resistance metallic contacts [6,8] or by bending the SWCNT with an atomic force microscope (AFM) tip [7], in order to decouple a section of the metallic SWCNT smaller than the electron coherence length. From a technological point of view it would be highly desirable if parts of the SWCNT could be electronically decoupled by tunneling barriers created by atomic defects. That this is possible in principle was demonstrated by the observation of confined electronic states in a metallic SWCNT due to backscattering on a defect near the end of the tube [11]. But here again the defect was an intrinsic one of unknown nature. Recently it was shown that the creation of strong electron scatterers by ion irradiation [12] on SWCNT seems to be another promising way to create intratube QD.

From this few examples it becomes evident that the understanding of the electronic modifications of SWCNT provoked by atomic defects and the controlled creation of such defects can be key points for the development of SWCNT based electronics. In this work we investigate the creation of defects on SWCNT by means of an electron cyclotron resonance (ECR) plasma of hydrogen. The characteristics of the ECR plasma are a high degree of ionisation and low kinetic energy of the produced H$^+$ ions. Earlier works on highly oriented pyrolytic graphite (HOPG) have shown the effectiveness of an exposure to create vacancy and chemisorption type atomic defects, where especially the vacancy type defects acted as strong electron scatterers [13-15]. In this work we characterise the topography and the STS signature of hydrogen ECR plasma induced defects on SWCNT.

2. Sample preparation and creation of defects

2.1. Control of the SWCNT density

In this work, as for all STM related works, the preparation of the sample is a key issue which however in literature is most often only discussed very briefly. For this reason we take the time to describe this point in more details here. At low temperature (5K) required for high resolution STS, the low temperature scanning tunneling microscope (LT-STM) scanning area is restricted to about only 1µm x 1µm in our case. Therefore the required density of individual SWCNT for LT-STM investigations should be between 1 and 10 tubes/µm$^2$. To avoid later undesirable contamination of the STM tip we must use SWCNT as pure as possible. Prof. Smalley’s group (Rice University, Houston, USA) kindly provided us SWCNT raw material produced by high pressure CO disproportionation process (HiPCo). The raw material was treated with a multistage purification method based on metal catalyzed oxidation [16]. In a first step we produce a SWCNT suspension out of the dry powder like raw material. We found the best results with 1,2-dichloroethane, in accordance with the most experiments on nanotubes reported in the literature. A SWCNT suspension is obtained by putting a little quantity of raw material in a vial containing about 1 milliliter of 1,2-dichloroethane. The right amount of SWNT in the solution is best controlled by the color of the suspension after sonication, which should be light grey when contained in a 10 mm inner diameter vial. In order to break the tube bundles we sonicated the suspension between 2 and 4 hours, where no significant differences in tube diameter and tube length distribution for the different sonication times could be observed. The solution was always tested on freshly cleaved mica, where the density of SWCNT was measured with tapping mode atomic force microscopy (TM-AFM) using a commercial Nanoscope III instrument. A very efficient way to obtain acceptable densities is to drive away the deposited drop of the light grey solution after a few seconds by blowing it off with pressured nitrogen. The solution must be deposited on the substrate direct after the end of the sonication process to avoid an aggregation of the SWCNT. This even though there is no change in the optical appearance as observed by naked eye of the suspension. Figure 1 displays the TM-AFM characterization of an optimal deposition procedure.
Figure 1. Dispersion of SWCNT on mica. TM-AFM image of SWCNT sonicated for 3 hours (a) and 4 hours (b) in 1,2-dichloroethane deposited on freshly cleaved mica. Diameter (c) and length (d) distribution for SWCNT sonicated for 3 hours

Figure 1a shows the 3x3 µm² TM-AFM image of SWNT deposited on freshly cleaved mica from a suspension sonicated for 3h. For the same solution, the resulting density is very sensitive to the deposition process, especially to the time elapsed between the deposition and the nitrogen dry blown. It is then difficult to reproduce several times the same density. It is also important to mention that it is difficult to obtain a homogenous density on the entire substrate (1 cm²).

A statistical study on SWCNT (with 3 hours sonication time) distributed in nine different TM-AFM images was performed. The resolution of TM-AFM is not accurate enough to differentiate individual SWNT and small bundles (two or three SWNT) but we could enumerate about 40% of apparently individual SWNT or small bundles and about 20% of large bundles (diameter > 1.5 nm). The rest are individual SWNT or bundles with non homogenous diameters along the entire tube. This is partly due to attached impurities like residual catalytic metal and amorphous carbon still present in the solution. The measured distributions are reported in figure 1 b) and c). The major part of the SWCNT length distribution is situated between 100 nm and about 2µm, with a maximum probability around 400-500 nm. The most frequently measured diameters are between 0.4 nm and 1.6 nm with a dominant peak between 0.9 nm and 1.1 nm. The average diameter of HiPCo individual SWCNTs produced at Rice University is approximately 1.1 nm [16] and therefore in good agreement with our measurements on the same kind of nanotubes.

2.2. Deposition of SWCNT on Au(111)

In way to perform STM measurements, we used gold on glass substrates commercially available from Arrandee [17]. The special borosilicate glass (1.1 mm thickness) is covered by a thin adhesive chromium layer (2.5 +/- 1.5 nm) and a final gold layer which is 250 +/- 50 nm thickness. The best quality of the surface was achieved with a first ex-situ hydrogen flame annealing, without letting the gold surface become bright red, followed by several sputtering and annealing cycles in-situ in the ultra high vacuum (UHV) preparation chamber of the OMICRON LT-STM used in this study. A typical process consists of three sputtering and annealing cycles, with decreasing duration times. Standard sputtering times are 40, 20 and 10 minutes. The annealing of the gold surface was performed at about 420-450°C for about 5-10 minutes for each cycle. A last annealing cycle at about 420°C was performed for a few seconds. STM analysis of the gold surface revealed atomically flat Au(111) terraces with typical hearing bone reconstruction.
The SWNT solution was first tested on freshly cleaved mica with TM-AFM in air. The deposition of the solution occurred ex situ, following the same process as described above for mica. The resulting SWNT densities are quite similar for the same solution on mica and on Au(111). The sample was then reintroduced in the preparation chamber at a pressure of about 10^{-10} mbar. To remove contaminates from the solvent of the SWNT suspension and due to the exposure to air the sample was annealed for a few minutes at 390° C prior to the STM/STS investigation.

2.3. Creation of low energy H⁺ induced defects

A 2.45 GHz ECR plasma source is fitted to the preparation chamber of the LT-STM facility. The source has a cylindrical 40 mm diameter cavity with a central, cylindrical 17.5 mm diameter antenna made of molybdenum. The magnetic field for the cyclotron resonance is created ex-situ by six permanent magnets. Typical plasma treatments were performed at a hydrogen pressure of about 8 \times 10^{-2} mbar and a microwave power of 60 W. The sample is positioned on a manipulator at about 6 cm under the plasma region and can be moved horizontally towards max 7 cm far from the antenna axis. The ion energy distribution measured with an electrostatic analyzer showed that 85% of the hydrogen ions are comprised in a narrow energy region around 1 eV and the maximum detected energy is \sim 16 eV. A typical ion flux measured at about 6 cm under and in the axis of the antenna lies in the order of 2 \times 10^{13} s^{-1} cm^{-2} [14]. We showed in an earlier work [13-15] that exposure of HOPG to the hydrogen plasma source described above mainly resulted in the creation of two types of defects: chemisorptions of hydrogen on the basal plane of graphite and carbon vacancies. These two types of defects led to a strong modification of the local electronic structure near the Fermi level and acted as strong scattering centers. Moreover, we know that SWCNT buckypapers irradiated under the same conditions contain chemisorption sites [14].

\[\text{Figure 2. STM current image of SWCNT deposited on Au(111) surface and treated with the hydrogen ECR plasma source. } U_s=1V, I_s=0.1nA, \text{ feedback gain}=3.96\%. \text{ Inset presents a topographic STM image with a linecut along a portion of a SWCNT with four defects.}\]

Irradiation tests were first performed on HOPG to determine the sample position and irradiation time parameters, in order to obtain later well adapted defect densities on SWCNT. At a position of about 3.5 cm off from the antenna axis and an irradiation time of about 1 second, large STM images (100nm x 100nm) of the treated HOPG surface revealed a mean number of stochastically distributed defect sites of about 70, giving a density of 0.7 \times 10^{12} cm^{-2}. We can reasonably suppose that for short irradiation times, each hydrogen ion will give rise to a defect with high probability. The lowering of the defect sites density of about a factor 30 compared to the ion flux measured at 6 cm under the plasma region is due to a strong reduction of the flux in the x-direction (3.5 cm).
2.4. STM and STS characterization and discussion

STM images were recorded in constant-current mode with the voltage applied to the sample. Figure 2 shows a typical large area topographic current image of plasma treated SWCNT, where the plasma induced defects can be seen as hillock-like features on the tubes. The density is comparable to the one determined on the HOPG for the same exposure. The inset in fig. 2 shows a topographic detail of a SWCNT with four defects and the corresponding line profile along the dash line in the STM image. The hillock-like defect features showed an apparent height between 1 Å and 2 Å. Similar apparent protrusions in the STM topography have been observed in the case of hydrogen plasma treated HOPG. Comparison with simultaneously performed AFM measurements, however, revealed that the protrusions in the STM were imaged as depressions in the AFM [13]. This raises the question whether the protrusions in the STM are due to a real structural modification of the SWCNT or to an electronic effect. To answer this question we have performed STS on the hydrogen plasma induced defects.

Figure 3 presents a first result obtained at a temperature of 77 K on a metallic SWCNT. Figure 3a shows the topographic image of two defects with the corresponding flattened image displayed in 3b. The consecutively numbered markers indicate positions, where single dI/dV spectra were recorded with the STM feedback loop turned off. The corresponding spectra represent in first approximation the LDOS. Spectrum 1 represents the LDOS of the clean tube with a non-zero LDOS at the Fermi energy indicating a metallic tube. The onsets of the first van Hove singularities (vHs) are spaced by 1.05 eV. On the defect itself we observed a single intense peak state at the Fermi energy as evidenced by the spectra 3-5. The flattened image in figure 3b shows that the presence of a peak at the Fermi level in the LDOS is confined on the defect site, which is also corroborated by the fact that very close to the defect the LDOS return to normal as evidenced by spectrum number 2. From this finding it seems reasonable that the hillock appearance of the defects in the STM topography is partly due to an
electronic effect of an increased density of states near the Fermi energy. An STS simulation based on
tight-binding Green’s function technique for the tip positioned on a single vacancy in a metallic
(10,10) SWCNT was reported in the literature [18] and is presented in figure 4d. The calculated
increase in LDOS near $E_F$ is due to the dangling bonds states close to $E_F$ spatially localized on atoms
near the vacancy. Deeper STS investigations are needed, but we can reasonably think that the
measured peak close to $E_F$ is due to the presence of a vacancy.

We showed that we are able to create and image low energy hydrogen ions induced defects on
SWNT with control on the defect density. This method is not invasive and permits very localized
modifications of the geometrical structure of the tubes. LT-STM topographic investigations revealed
hillock-like features with heights between 1 Å and 2 Å on defect sites. STS measurements showed a
strong modification of the LDOS close to the defects. Further deeper investigations in the
spectroscopy are needed to understand the exact nature of the defects and also their effects on the
electronic properties of the SWCNT.

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