STM imaging of carbon nanotube point defects

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Carbon nanotube defects can play important role in the applications since their presence affect mechanical [1] and transport properties [2]. Topological point defects (e.g. non-hexagonal carbon rings) can form during the nanotube growth process or they can be introduced after synthesis for example by chemical purification or irradiation. In this work we investigated nanotube point defects created by ion irradiation. Multi-walled carbon nanotubes produced by the arc-discharge method were dispersed on HOPG surface and irradiated with Ar$^+$ ions of 30 keV. We used a low dose of $D = 5 \times 10^{11}$ ions/cm$^2$ in order to create individual, non-interacting defects. The arc-grown nanotubes are generally straight tubes and they accumulate very few defects during synthesis in comparison with the catalytically grown nanotubes [1].

STM investigations revealed that the nanotube defects created by irradiation appeared as hillock-like features (Fig. 1b) similar to the hillocks observed earlier on irradiated HOPG [3]. These hillocks could not be observed on the non-irradiated nanotubes (Fig. 1a).

In order to study the origin of the observed hillocks, we performed both STM and contact mode AFM measurements on the irradiated HOPG substrate. The measurements showed that 100 – 105 hillocks could be imaged on an area of 100x100 nm$^2$ by STM (Fig. 2a), while only 9 – 10 hillocks could be detected on a same size area by AFM (Fig. 2b).

Figure 1. STM images of multi-walled carbon nanotubes before (a) and after irradiation (b). The hillock-like features in (b) are the signatures of the irradiation induced defects.

Figure 2. STM (a) and contact mode AFM image (b) of irradiated HOPG substrate.
These results show that the major part (~ 90 %) of the hillock-like protrusions seen by STM is due to the change in the local electronic density of states (LDOS), and only a small part (~ 10 %) can be attributed to clusters and deformations topographically emerging from the HOPG surface. Due to the graphitic structure of multi-walled nanotubes it is reasonable to assume a similar ratio for the hillocks observed on the nanotube surfaces. The major part of the hillocks can be ascribed mostly to vacancies, since at this ion energy the nuclear stopping dominates over the electronic stopping. Furthermore, according to simulations vacancies appear as hillocks on the STM images [4].

We observed hillock-like protrusions not only on the STM images of irradiated nanotubes but also during the STM investigation of coiled carbon nanotubes (Fig. 3b). Figure 3a) shows a coiled nanotube synthesized by the decomposition of fullerenes [5], with 3.5 nm between the coils.

![Figure 3. STM images of a coiled carbon nanotube. The image in (b) shows a magnified portion from (a). The hillock-like features in (b) are attributed to non-hexagonal carbon rings.](image)

Figure 3b) shows a magnified portion from Fig. 3a), where one can observe the hillock-like features which appear repeatedly and in a regular way along the coils. These features are attributed to the non-hexagonal carbon rings which are responsible for the bending and coiling of the nanotubes. Theoretical works show that non-hexagonal carbon rings incorporated in a hexagonal structure also appear as hillocks, because they change the LDOS by introducing additional electronic states near the Fermi level [6, 7]. The regular appearance of the hillocks along the coils agrees well with the early model structure proposed for coiled nanotubes [8].

**References:**

[6] V. Meunier, Ph. Lambin, Carbon **38** (2000) 1729

TNT2006 04-08 September, 2006 Grenoble-France