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Characterization of surfaces of carbon fibres by scanning tunneling microscopy

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SUMMARY

The experimental results obtained by scanning tunneling microscopy (STM) studies of different carbon fibres are presented and discussed. The comparative analysis of the STM images at scales from hundreds of nanometers down to atomic scale reveals the differences of surface features for carbon fibres processed from different precursors, polyacrylonitrile fibres and pitch. The high temperature treatment of carbon fibres - the so-called graphitization process - as used to improve the stress modulus induces drastically increased ordering phenomena at the atomic level. Structural information obtained by STM on the surface of the fibres as well as in their cross sectional areas is discussed in comparison with known results of diffraction studies. STM appears to be the new powerfull technique for the detailed structural studies of surfaces of carbon fibres. The perspectives of these studies are under discussion.

INTRODUCTION

With the appearence of STM 1) the possibilities of surface studies of conductive and semiconductive materials have increased enormously 2). The visualization of surface structure features down to atomic scale, provided by STM, has overcomed the resolution limits of other electron microscopic techniques. But even on comparable scales STM is advantageous, definitely, in sensitivity to surface corrugation when compared with scanning electron microscopy (SEM). Due to the exponential dependence of tunneling current on the distance between the diagnosting metallic tip and the examined surface, the STM sensitivity in z-direction, perpendicular to surface, is reaching values of 0.01 Å, far beyond the limits of SEM resolution 3).

The perfectly flat surface of monocrystals of highly oriented pyrolytic graphite (HOPG) and its conductivity make this material very attractive for STM applications. Thus, HOPG is a compound extensively studied, and it is used as the standard for testing the quality of tips and instrumentation. The STM images of graphite present the surface charge density distribution which corresponds to the atomic structure of the surface. The high resolution graphite image shows six-membered rings of charge density patterns with characteristic distances identical to the crystallographic data. Three of six "hills" - with a distance of 2.46 Å - appear more pronounced in STM images in most of the studies. This phenomenon is still under investigation 4). Figures 1 present our top view and threedimensional images of HOPG, which lack of pronoun-

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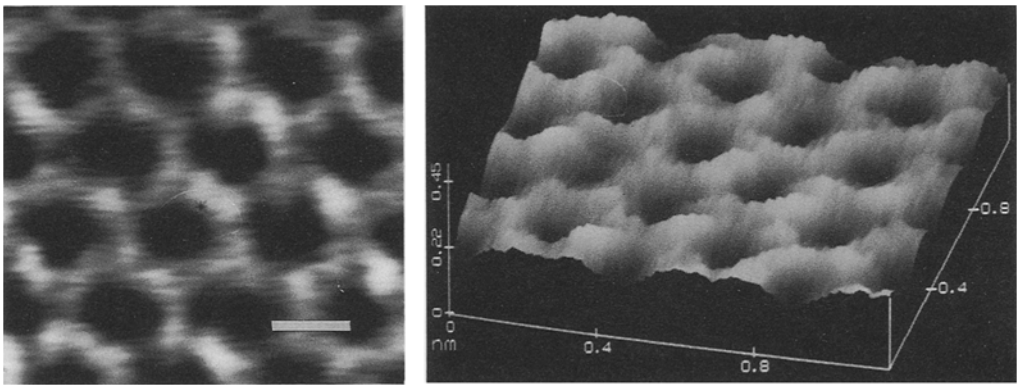


Figures 1: Pyrolytic graphite, tunneling current 1.0 nA, bias voltage 30 mV
Left top view image A , bar = .2 nm Right threedimensional plot B

ced inequivalence of the "hills". Though final understanding of STM imaging is not achieved even for well studied systems, like graphite, the applications of STM are widespreading.

Naturally STM was applied for studies of different types of carbon materials 5) but the generalizations are not yet done. Different types of surface defects like steps, missing atoms and adsorbates which were distinguished by STM on HOPG surface also can be visualized on other type carbon surfaces.

In this paper results of the STM approach to surface characterization of carbon fibres are presented and discussed. The general applicability of the method already was approved 6). Comparative analysis of surface features of carbon fibres from different precursors and after different temperature treatment, however, should be emphasized in the following report. It is well known that many important properties of carbon fibres which are realized in polymeric composite materials are strongly dependent on surface structure 7). The main factors, which influence surface features, are the nature of the precursor and the approach of conditioning. Strength improvement, for example, is achieved by high temperature treatment of the carbon fibre, which leds to graphitization. This process is an energy consuming one, and its optimization asks for knowledge of correlations between surface structure and high temperature treatment. In order to study the capabilities of STM in the examination of carbon fibres we have chosen the materials from two precursors, and with different thermal history. STM images of surface areas with scales from hundreds of nanometers to few nanometers are obtained and discussed, for carbon fibres of different origin.

EXPERIMENTAL

Four different types of carbon fibres were studied. The commercial T300 - PA-LT - and M40 fibres - PA-HT - (Toray, Japan) are obtained from polyacrylonitrile fibers as a precursor. They are known as low and high modulus fibres, resp., and they differ from each other by the temperature of treatment (1500^{o} C and 2500^{o} C, resp.). Two other fibres - PI-LT and PI-HT - are obtained from pitch. They also were treated at dif-

ferent temperatures, the PI-HT fibre at the higher one. Single fibers as fixed on metallic support by silver glue were used for the STM studies.

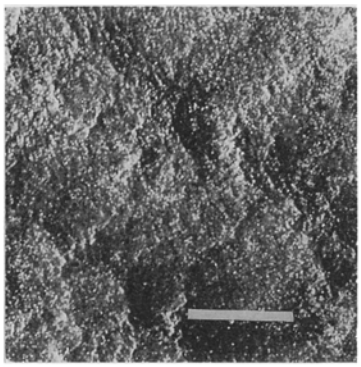
For the STM experiments the commercial microscope Nanoscope II (Digital Instruments Inc., Santa Barbara, Cal/USA) was applied at ambient conditions. The piezo-

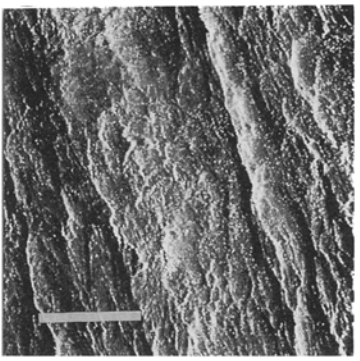
head type "A" allows a maximal scanning area 380 x 380 nm. The quality of tips as cut mechanically from Pt(70)/Ir(30) wire was checked on a monocrystal of HOPG. We used tips which exhibit an accuracy in x,y surface directions better than 0.1 Å while measuring the distance between "hills" representing carbon atoms of graphite rings. Tip was positioned close to surface of the carbon fiber with the help of an optical microscope. The final travel of the tip to a distance of approximatelly a few Å, at which the set-point tunneling current was detected, is achieved with computer controlled stepper motor. During scan over the surface the tip follows the threedimensional profile of constant tunneling current. Current imaging mode was used in all experiments. The images are usually presented as top view pictures in which more brighter patterns correspond to more remote position of the tip with respect to the sample surface, in z direction. The parameters applied are: Tunneling current 1 - 2 nA, bias voltage 30 - 60 mV. These parameters are close to those usually used for imaging HOPG. For large scales (hundreds of nanometers) the scanning frequency was 0.5 Hz, and for small scales (few nanometers) 19, 26 or 39 Hz, resp. Arrays of 400 x 400 points were used for presentation of top view patterns. The only filtration procedure applied to images at atomic scale was the removal of noise in y direction which corresponds to surface features smaller than 1 Å. The large scale images are unfiltered.

RESULTS AND DISCUSSION

In Figures 2 A-G and 3 A-G the STM characteristics of the surfaces of all fibres are presented. The large scale STM images (330 x 330 nm) of different are compared in the first row of Figs. 2 A-B (pitch based fibres PI-LT and PI-HT) and of Figs. 3 A-B (PAN based fibres PA-LT and PA-HT). These images reveal the topology features, which demonstrate the roughness of carbon fibre surfaces. The differences in the STM images of carbon fibres are evident. The high temperature treatment of pitch-based fibre leds to more developed surface morphology (Fig. 2 B). The striations on the PI-HT fibre surface are oriented parallel to fibre direction. Further, the identically oriented ca. 2 nm deep valleys are randomly distributed on this surface. One may distinguish more fine details on large scale STM pictures. The surface filaments with a width in the range 10 - 20 nm are oriented parallel to the main direction.

Two points should be underlined in the analysis of microtopology of carbon fibres processed from a PAN precursor. The longitudial striations, which can be easily detected on the surface of the PA-LT fibre (Fig. 3 A) were not found on the high temperature treated PA-HT fibre surface (Fig. 3 B). Thus the latter treatment makes surface smoother. Another point to be mentioned is the orientation of surface filaments with width in the 10 - 20 nm range, which are well distinguished on the PA-HT fibre. They are oriented at an angle around 30^{o} with respect of fibre direction. This finding is in contrast to the surface structure of pitch-based fibre, PI-HT. The observed surface filaments may be the crystallites as revealed in diffraction studies 7).



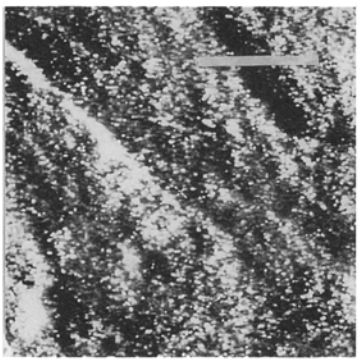


Figures 2: LT and HT treated pitch based (PI) carbon fibres

Tunnel current 1 nA
Bias voltage 60 mV
Top view images
330 x 330 nm
Bar = 100 nm

A • PI-LT

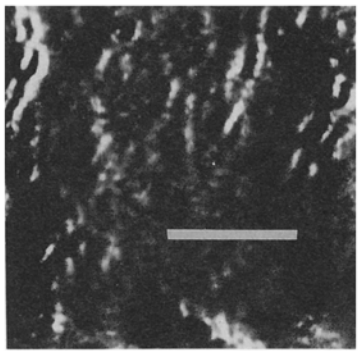
PI-HT • B

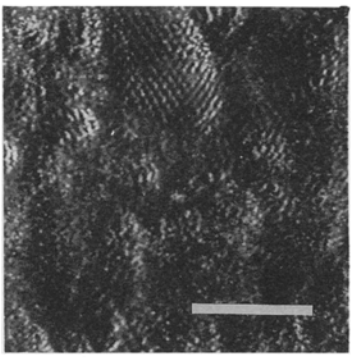


Tunnel current 1 nA
Bias volt. 60/50 mV
Top view images
27 x 27 nm
Bar =10 nm

C • PI-LT

PI-HT • D



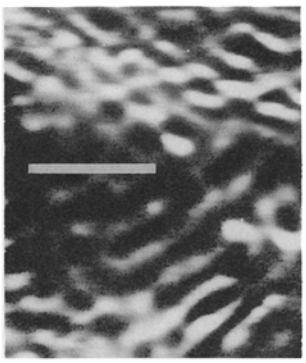


Tunnel current 1 nA
Bias volt. 30/50 mV
Top view images
5.2 x 5.2 nm
Bar = 2 nm

E • PI-LT

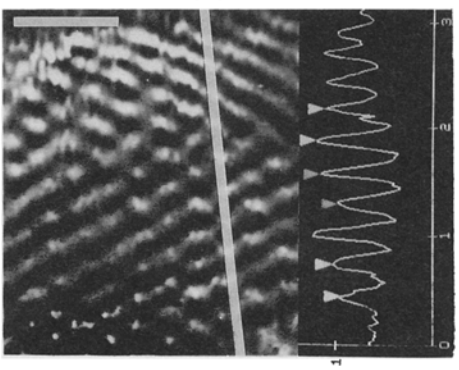
12 x 12 nm
Bar = 4 nm

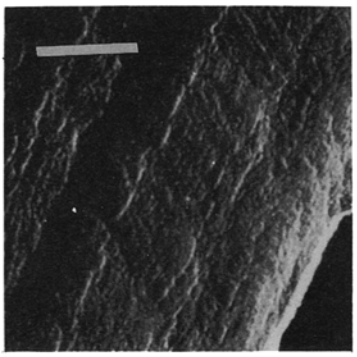
PI-HT • F



Tunn. curr. 1/2 nA
Bias v. 50/31 mV
Top view images
2.7 x 2.7 nm
Bar = 1 nm

G • PI-HT • H





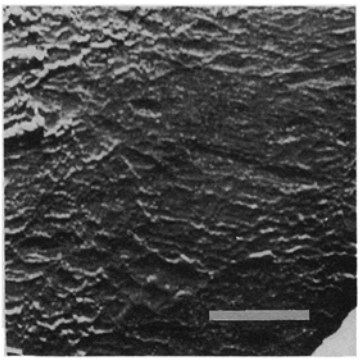
Figures 3: LT and HT treated PAN based (PA) carbon fibres

Tunnel current 1 nA
Bias voltage 60 mV

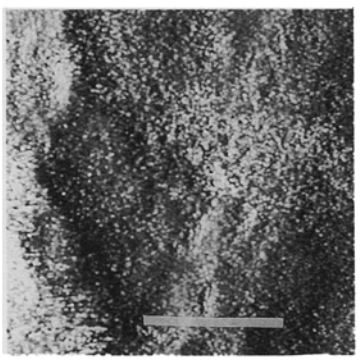
Top view images
330 x 330 nm

Bar = 100 nm

A • PA-LT



PA-HT • B



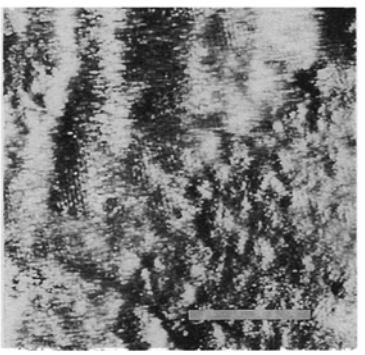
Tunnel current 1 nA
Bias volt. 30/60 mV

Top view images
20 x 20 nm
Bar = 8 nm

C • PA-LT

27 x 27 nm

Bar = 10 nm



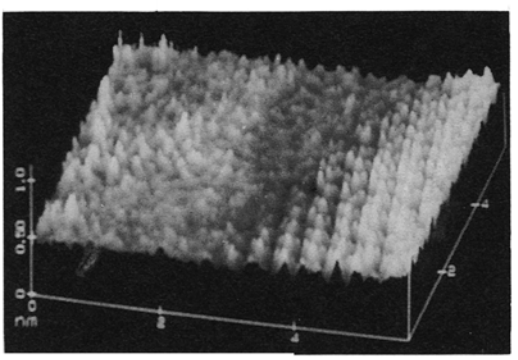
PA-HT • D

Tunn. c. 1 nA
Bias v. 60 mV

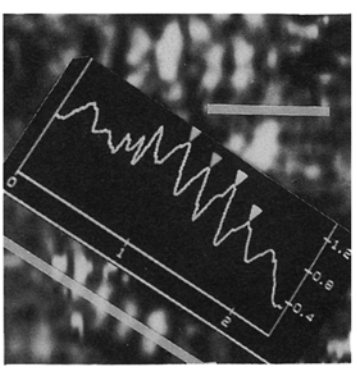
Top view
10.4 x 10.4 nm
Bar = 4 nm

E • PA-LT

3 - dim. view
6.0 x 6.0 nm



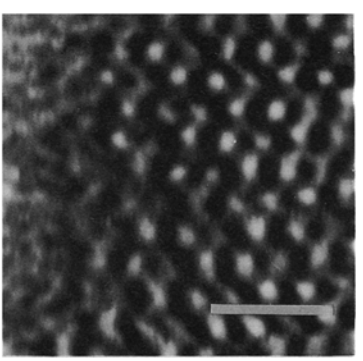
PA-HT • F



Tunnel current 1 nA
Bias volt. 30/60 mV

Top view images
2.6 x 2.6 nm
Bar = 1 nm

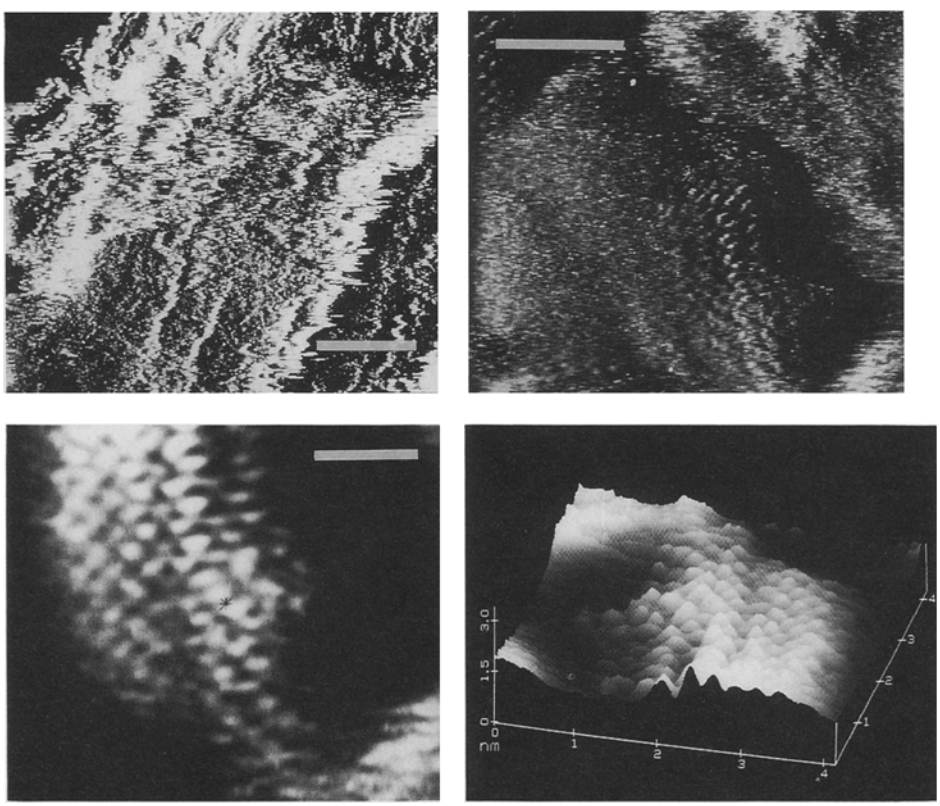
G • PA-LT



PA-HT • H

The differences in the surface features caused by high temperature treatment become more drastically evident, when the STM studies are conducted on smaller areas, from 27 x 27 nm down to 2.6 x 2.6 nm. This statement is well demonstrated by Figs. 2 C-H and 4 C-H. The STM images of the PAN based PA-LT fibre are presented in Figs. 3 C, E and G. In some regions one can distinguish the traces of atomic scale structure. In 3 G their electronic profile is given additionally. The local periodicity of surface electron density patterns in these places is near 2.5 Å. This parameter is close to that, which characterizes the periodicity observed in well ordered STM images of the main crystallographic plane of HOPG. Much more ordered surface regions were detected for the "high temperature" PA-HT fibre. The atomic order can be easily seen even in the 27 x 27 nm image (Fig. 3 D). Best ordered places of this type - as visualized in Fig. 3 H - exhibit quite perfect atomic level structure similiar to that observed on HOPG surface. The threedimensional view of such an area (Fig. 3 F) shows the contrast of a graphitized elevated region to a less structured lower part.

The observed influence of temperature treatment to atomic scale details on carbon fibre surface is confirmed also for the pitch based PI-LT and PI-HT fibres, in Figs. 2 C, E, and 2 D, F, G, H, resp. As in the case of PAN based PA-LT fibre the surface featu-



Figures 4: Cross sections of pitch based carbon fibre PI-HT - top view images - Tunneling c. 1.0 nA - A - bias v. 400 mV - bar = 100 nm - B - bias v. = 162 mV - bar = 2.0 nm - bias v. = 162 mV - C - bar = 1.0 nm - D - threedimensional plot

res of the pitch based PI-LT fibre (Figs. 2 C and E) reveal only traces of atomic scale order. The periodicity constant is bigger, however, than for the PA-LT fibre. Its averaged parameter (3.3 Å) is close to the interplanar distance in a graphite monocrystal.

The atomic surface order of high temperature treated PI-HT fibre is evident at 27 x 27 nm areas (Fig. 2 D). As in the case of the PAN based PA-HT fibre the ordered atomic structure preferably is observed on elevated surface parts. The surface of prolonged crystallites with width of several nanometers shows two various types of atomic structure on the PI-HT fibre surface. In the upper part of the surface given in Fig. 2 F one can distinguish large atomically ordered domains. The graphite-like hexagonal structure of this region is emphasized in Fig. 2H where the electronic profile is given additionally. In other parts of this surface a curved chain structure was detected (Fig. 2 G). The periodicity constants of patterns in the graphite-type structure are a little higher than in HOPG. Thus the identification of the best ordered regions on surface of PI-HT fibre as the monocrystal structure should have additional experimental support. The distances between neibouring chains are near 0.25 nm. This type of structure was already observed in one of carbon materials 5) but it is not yet explained.

STM images of cross-sectional areas of PI-HT fibre are presented in Figures 4 A-D. The large scale image, A, visualizes the topography of the fracture surface. The small scale images, B, C and the three-dimensional view D, demonstrate that atomic ordering after high temperature treatment happens inside of carbon fibres as well as on the surface. The regions with the graphite like structure can be distinguished in several places.

Experimentally the STM studies of cross sectional areas of carbon fibres are more difficult because the tip should be engaged in relatively small regions. The diameter of such fibres is around 8 μm. The best choice of instrumentation for further studies is the combination STM- SEM.

CONCLUSIONS

The presented STM results definetely show that this new method is very important for studies of surfaces of carbon fibres. The surface features of varying areas can be analyzed. The structural differences at various scales were determined for carbon fibres, obtained from PAN fibres and from pitch. Drastical improvement of atomic scale order was detected as the result of high temperature treatment of carbon fibres from both precursors. Generally, the order is more developed in PAN than in pitch based carbon fibres, in parallel to the differences in the mechanical properties. Thus, STM may be used succesfully for the control of the graphitization process, and for technological control, consequently.

Further, the visualization of atomic structure on carbon fibre surface and on its cross sectional areas permits to describe the graphitization process in more detailed way. Different atomic structures observed on the carbon surface should encourage deeper understanding of solid state reactions. Also the possibilities of STM analysis of cross-sectional areas as well as of surface modifications after physical and chemical treatment are evident. Corresponding studies are in progress.

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