First Scanning Tunnelling Microscopic Observations of Carbonaceous Films on a Quartz Substrate not having a Complete Graphite Structure

Kazuhisa Murata,* Morio Yumura, Hisashi Ueda, Hisakazu Nozoe and Yasujiro Kawabata
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japan

Scanning tunnelling microscopic (STM) observation of the carbonaceous film prepared by direct pyrolysis at 950 °C of cyclododecane demonstrates an irregular array of carbon atoms (of benzene rings) relative to graphite; this provides the first STM results for carbonaceous compounds not having a complete graphite structure.

Much interest has been shown in carbonaceous materials prepared by pyrolysis of organic substances at a temperature of *ca.* 1000 °C, because the materials are very stable in air and are expected to show not only electron conductivity, but also magnetic properties due to their incomplete graphitized structure involving many unpaired electrons.[1–3] In the present work, in order to obtain information on the structure of such carbonaceous materials, scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) have been used, in addition to other methods such as electrical conductivity measurements and laser-Raman analysis.

The carbonaceous sample was formed on a quartz substrate (8 × 6 mm). Commercially available cyclododecane was used as the carbon source. Both the cyclododecane and the quartz were placed separately in a quartz tube, which was evacuated overnight. The quartz substrate was heated at 950 °C, contacted with the monomer and the monomer rapidly pyrolysed, being deposited on the substrate. The reaction time was 1 h. The quartz tube was cooled and the resulting carbonaceous film on the substrate was taken out and various measurements were made.

X-Ray diffraction analysis of the carbonaceous film showed

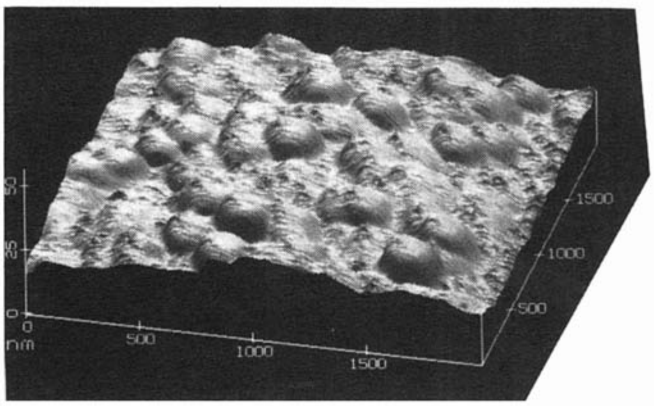

Fig. 1 AFM image of the carbonaceous film on a quartz substrate: 2000 × 2000 nm three-dimensional oblique view

(a)
(b)

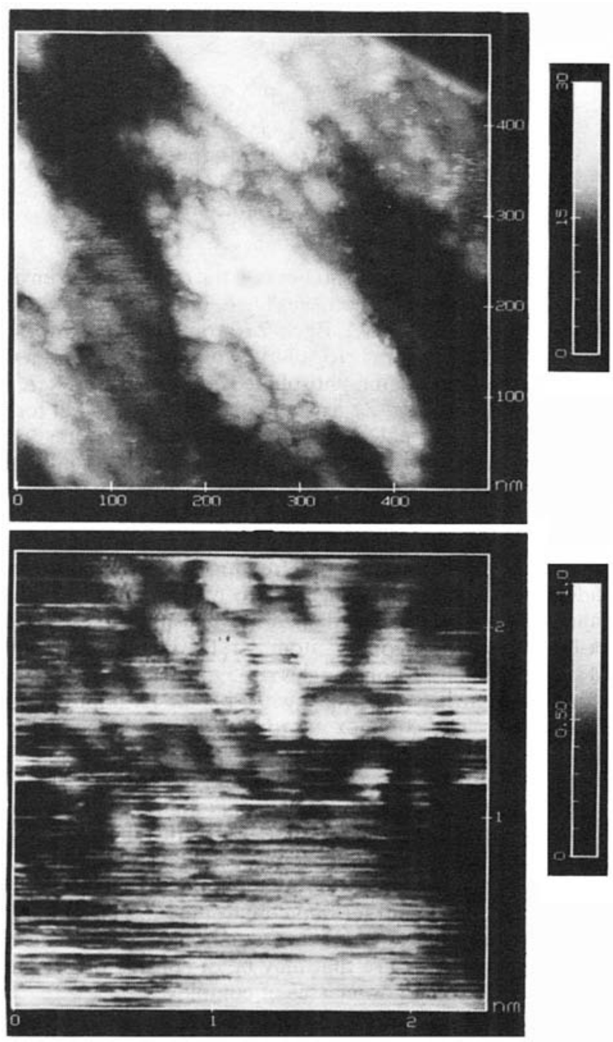

Fig. 2 STM image of the carbonaceous film on a quartz substrate (bias voltage +20.1 mV; setpoint current 0.32 nA): (*a*) 500 × 500 nm top view; (*b*) 2.38 × 2.38 nm top view at higher magnification

no distinct crystalline phase, only an amorphous phase. The absorption spectra of the film exhibited only a broad band with a maximum at around 285 nm spread over the whole region scanned.[4] Only a very weak absorption at 1580 cm^{-1} was observed by laser-Raman analysis.[5] Its electrical conductivity, measured by a dc four-probe method using silver paste as electrodes on the film surface with a gap distance of 1.5 mm, was 760 S cm^{-1} at room temperature and 580 S cm^{-1} at 77 K, lower for graphite itself.[6] These findings are consistent with an incomplete graphitized structure.

Since the films were air-stable, STM and AFM observations were performed in air at room temperature using a Nanoscope II (Digital Instruments) microscope mounted on a vibration isolation table. An electrolytically etched tungsten tip and silicon nitride tip were used for the STM and AFM observations, respectively.

Fig. 1 shows a three-dimensional oblique view of a low-magnification (2000 × 2000 nm) AFM image of the carbonaceous film; Fig. 1 shows that the film consists of a structure with irregular bumps. For comparison, an AFM image of the quartz substrate alone showed no such structure.

Fig. 2(*a*) shows a macroscopic STM image (500 × 500 nm) of the same sample. As expected from the AFM observations, an uneven, rugged structure with several corrugations appears. Fig. 2(*b*) shows a higher-magnification view (2.38 × 2.38 nm) of a brighter part of the imaged surface extending obliquely in Fig. 2(*a*). There are many ellipsoidal and/or circular features, especially in the upper half of Fig. 2(*b*). The brightness of each feature is not the same. The mean distance (*ca.* 0.256 nm) between any two adjacent spots is very close to the usual atomic spacing of graphite (a = 0.246 nm).[7] No such images could be seen in any area for the quartz substrate only. One possible explanation for these observations is that each spot represents a carbon atom in an irregular array of benzenoid rings indicative of an incomplete graphite structure, consistent with the results from X-ray diffraction, electrical conductivity and magnetism[1–3] measurements described above.

To our knowledge, this is the first report concerning STM observations of carbonaceous films not having a complete graphite structure,[8] although some reports have been published about STM observations on highly oriented pyrolytic graphite (HOPG).[9]

The following possibilities have to be considered. (*i*) Since the STM (AFM) images were recorded in air, some gas or liquid could be adsorbed on the surface; (*ii*) contacting of the surface by the STM (AFM) tip could be the origin of these STM images. However, the images observed here were seen only for the carbonaceous sample on the quartz substrate and are not seen for the quartz alone. The macroscopic view of the AFM (Fig. 1) should show a resemblance to the scanning electron micrograph of the same sample, usually obtained under vacuum; studies are in progress on this point. The images were reproducible for many scans, however, and we feel it is likely that the images originate from the structure of the carbonaceous film. STM studies in vacuum are the next step.

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