"Oxide-free" tip for scanning tunneling microscopy

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We report a new tip for scanning tunneling microscopy and a tip repair procedure that allows one to reproducibly obtain atomic images of highly oriented pyrolytic graphite with previously inoperable tips. The tips are shown to be relatively oxide-free and highly resistant to oxidation. The tips are fabricated with graphite by two distinct methods.

Scanning tunneling microscopy (STM) is based on the phenomenon that electrons can tunnel across the potential barrier established when two electrodes, in this case a sharp tip and a conducting or semiconducting surface, are approached within less than a nanometer.[1,2] The unique sensitivity of STM results from the exponential dependence of the measured current on the tip-sample separation. The sharpness of the tip is believed to be one factor affecting the resolution of the STM image.[3]

The exact role of the tip structure in STM is of yet an unresolved question. Although various studies of the tip structure and STM image have been performed,[4,5] correlation between the actual geometry and experimental STM results has still not been fully established. STM tips have been fabricated from metal wires such as tungsten (W) that can be electrochemically etched[6] or sharpened by grinding to achieve a radius of curvature less than 100 nm. While the etching procedure is straightforward and the resultant tips are fairly reproducible, the tip composition can vary depending on the purity of the starting material and contamination from the air and electrochemical bath. The usual contaminants are metal oxides,[7] organic adsorbates, and alkali metal salts and have been confirmed by scanning Auger microscopy and energy dispersive x-ray analysis.

While the preparation and cleaning of the sample surface have been important in most STM experiments to date, the tip preparation and cleaning procedures have been qualitative at best. Processing of prepared tips includes sputtering,[7] indirect electron bombardment,[8] field desorption/evaporation,[9] or controlled (or uncontrolled) tip crashes against the surface.[10] These procedures may crack the native oxide, transfer materials from the surface to the tip, or reform the atomic structure of the tip in such a way as to produce an atomically resolved STM image. However, this image is often short lived due to the delicate and seemingly dynamic structure of the tip. Presently, a good tip is merely defined as one which gives a highly resolved image without reference to the actual tip structure.

Because an oxide-free tip would be ideal for use in STM (oxide contamination creates an insulating layer which affects the tunneling barrier height), we have developed a STM tip that has very little native oxide and is highly resistant to air oxidation. In addition, the tip material is readily available and extremely inexpensive. The tip does not require sharpening or etching to produce atomically resolved STM images of highly oriented pyrolytic graphite (HOPG).[11] The tip is fabricated from a mechanical pencil lead which consists mainly of graphite.

We have been investigating the mechanism for the enhanced resolution of STM images of HOPG. In the process, when trying to simulate tunneling between two (sliding) graphite planes,[5,12] we discovered that a pencil lead as the tip readily produces atomically resolved STM images of HOPG.

The carbon tip is made by breaking a small piece of 0.5-mm-diam pencil lead just before use in the STM. Electron micrographs of a used carbon tip (obtained on an ETEC Auto Scan Electron Microscope with a 20-keV electron beam) are shown in Fig. 1. The end of the tip is fairly blunt

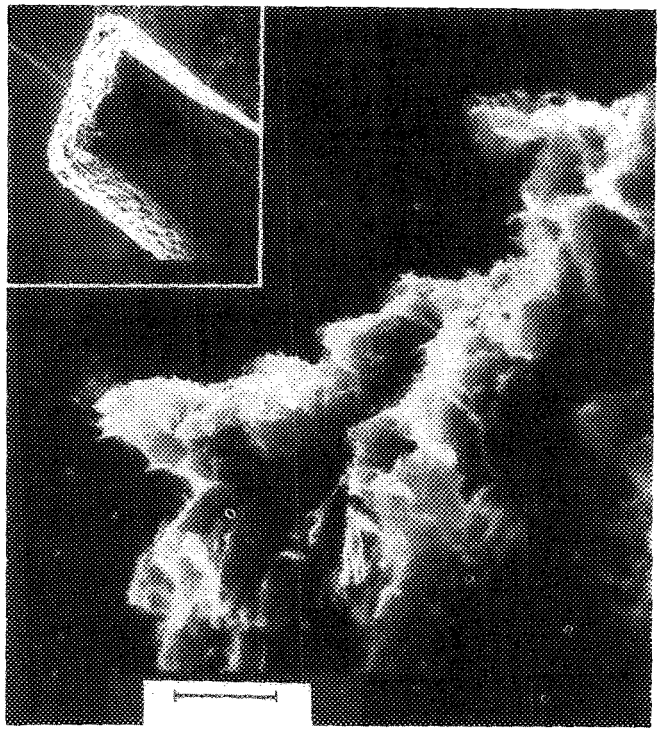

FIG. 1. Electron micrographs of a pencil lead tip (the bar scale corresponds to 5 μm). Insert shows tip at ten times less magnification.

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(Fig. 1 insert) and many times the diameter of electrochemically sharpened tungsten tips (see Fig. 3 insert). The end of the tip has been magnified 2000 times and is shown to consist presumably of small crystallites of graphite. The exact size of the crystallite from which tunneling occurs is unknown, but the crystalline nature of the graphite in the pencil lead was confirmed by x-ray diffraction.

The surface of the pencil lead as determined by x-ray photoelectron spectroscopy (XPS) is composed mainly of carbon and smaller amounts of oxygen and silicon. The carbon to oxygen ratio (elemental concentration in atomic percent) is around 15:1. (The carbon and oxygen content of the pencil lead is similar to that found for HOPG which had been cleaved and stored in air.) In addition to the low oxygen content of the carbon tip, the carbon should also be extremely resistant to further oxidation, particularly at room temperature.[13]

The STM image of HOPG shown in Fig. 2 was obtained with the carbon tip. The instrument used is described elsewhere.[14] These results were collected in the fast scan mode at room temperature in air without the feedback circuit. The scan speed of the tip is 250 Hz in the x direction and 5 Hz in the y direction, which produces five images/second. The images were recorded from the screen of a variable persistance oscilloscope by a VCR camera. The image shown in Fig. 2 (and Fig. 4) is a photograph of a single VCR frame of the CRT display monitor. No filtering of the images was done.[15] The size of the image in Fig. 2 is 2.1×1.2 nm. The sample-tip bias is about 100 mV. The average tunneling current is about 10 nA while the peak to valley variation is about 4 nA.

In addition to the development of the carbon (pencil lead) tip, we have also developed a tip repair method which restores used or damaged tungsten tips and enables them to produce atomic images of HOPG. The method involves coating a used tungsten tip with graphite. In practice, the used tungsten tip is dipped into a colloidal suspension of graphite in water (Aquadag Colloidal Graphite, Ted Pella, Inc., Tustin, CA). Alternately, a tip that is already mounted in our STM is coated using a capillary tube filled with the colloidal graphite.

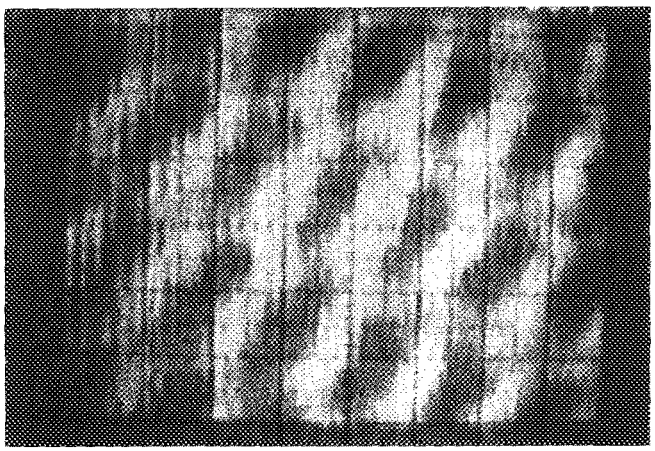

FIG. 2. STM image of HOPG taken in the fast scan mode with a pencil lead tip. The sample-tip bias is 100 mV. The average tunneling current is about 10 nA and the peak to valley variation is about 4 nA. The image size is around 2.1×1.2 nm and the sample bias is -200 mV.

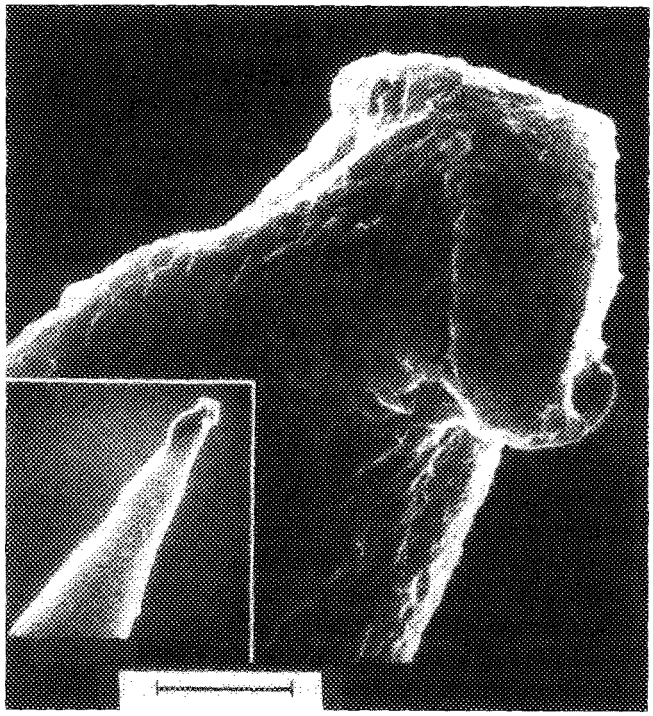

FIG. 3. Electron micrographs of a used tungsten tip coated with colloidal graphite (the bar scale corresponds to 5 μm). Insert shows tip at tens times less magnification.

Figure 3 shows an electron micrograph of a used ac-etched tungsten tip coated with colloidal graphite. A bend in the end of the tungsten tip is clearly visible (see insert) and was formed when the original tip made contact with the surface. The colloidal graphite coating on the end of the tip appears relatively featureless and much smoother than the surface of the pencil lead (compare Figs. 1 and 3—note the equivalent scales). X-ray diffraction confirmed the crystalline structure of the colloidal graphite coating.

The surface of the colloidal graphite is composed mainly of carbon and smaller amounts of oxygen and nitrogen. The colloidal graphite has a carbon to oxygen ratio of around 6:1. The oxygen content is roughly twice that found in the pencil lead and is due primarily to a higher concentration of an oxidized carbon species. Regardless of the higher oxygen content, the colloidal graphite is also expected to be highly resistant to further oxidation at room temperature.[13]

Figure 4 shows an STM image of HOPG obtained after coating a used tungsten tip with the colloidal graphite. The uncoated tungsten tip could not produce an image of HOPG. The size of the image is approximately 1.5×0.9 nm. The sample-tip bias is about 20 mV. The average tunneling current is about 48 nA and the peak to valley variation is about 3 nA. The scan parameters are equivalent to those described for Fig. 2.

After repetitive tests, we have *never* failed to achieve atomically resolved STM images of HOPG using either the pencil lead or colloidal graphite coated tips upon the initial approach. Tip "crashing" is not required to obtain these images. How these tips interact with the HOPG surfaces to produce these highly resolved images of HOPG is a matter of

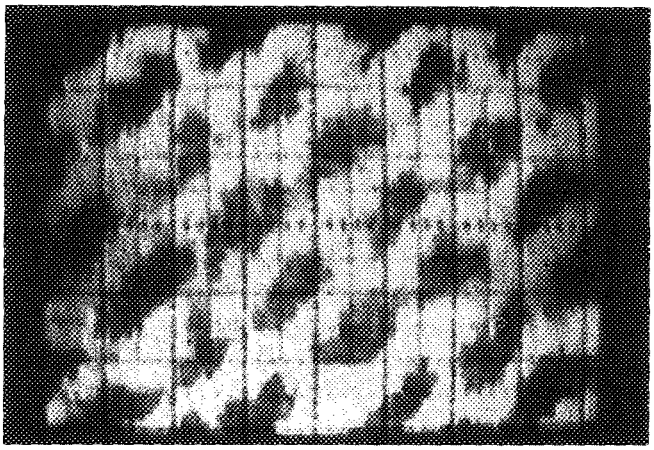

FIG. 4. STM image of HOPG taken in the fast scan mode with a used tungsten tip coated with colloidal graphite. The sample-tip bias is about 20 mV. The average tunneling current is about 48 nA and the peak to valley variation is about 3 nA. The image size is about 1.5×0.9 nm and the sample bias is -500 mV.

study in our laboratory and will be reported in another paper.

In conclusion, we have found a simple and reliable tip material, namely, pencil lead, and a tip repair method that routinely gives atomically resolved STM images of HOPG. The tips are stable in air and relatively free of oxide. In addition to the advantages gained in tunneling from or to an oxide-free material, the simplicity of this tip preparation and repair procedure will enhance the utility of STM.

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