Mechanism for the Nanometer Scale Modification on HOPG Surface by Scanning Tunneling Microscope*

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A technique applying voltage across the tunnel junction for writing permanent features on graphite with lines about 10 nm width using our home-built scanning tunneling microscope has been presented. Multiple-tip effects while modifying the surface are often met. The phenomena are explained in terms of the strong electric field existing at the junction between the tip and the surface. In addition, the shape of the structure indented by the tip is in agreement with that of the tip.

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In the past several years, scanning tunneling microscope[1] (STM) has been developed into an imaging method with diverse possibilities for real-space imaging on a scale which extends to atomic dimensions.[2] In many applications, its primary role is to perform a local experiment in which imaging is used primarily to select and define the location of the experiment. In other applications, it can be used as a tool for nanometer fabrication on the surface because of its advantages.[3] Nanometer-scale surface modification has important potential practical applications in areas such as high resolution lithography for solid state devices or high density data storage, and also is of fundamental interest in the study of mesoscopic physics (the regime between atomic sizes and microsizes). Some recent STM experiments have demonstrated the potential power of STM for modifying surface structures in the nanometer regime.[3–5] However, so far, the mechanism responsible for structure formation is not well understood. Additional studies are needed to explore new systems and to understand the physics of the modification process in greater detail. In this letter, examples of multiple-tip effect[6] in the surface modification were given, and strong electric field existing in the junction between the probe tip and the sample played a dominant role while indentating the surface.[7,8]

The instrument used in these experiments was home-built CSTM-9000 STM operated under atmospheric conditions.[9] Tips were prepared by mechanically cutting platinum iridium alloy wire. Samples of highly oriented pyrolytic graphite (HOPG, 6×6×1 mm) were cleaned immediately before loading in the STM. All images we obtained were in the constant-current mode. The experiment process could include two steps following. At first, The STM tip went along the route and positioned which could be realized with atomic precision controlled by a computer. In the meantime, a voltage pulse of variable width and amplitude completely controlled by the computer as well was applied across the tunnel junction at the positioned sites. The high voltage pulse would induce HOPG surface change because of chemical or physical mechanism so that an indentation could be left on the surface. And the second, the modificated surface was imaged by the same tip. The pulse amplitude necessary to write patterns on the surface

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varied from the tip to tip and ranged from 3 to 6 V. Pulse widths between 0.5 and 15 ms were used. While imaging the surface, the tunneling current and gap voltage were in the ranges of 0.1–0.5 nA and 0.2–0.5 V, respectively. The voltages were quoted with the sample positive with respect to the tip.

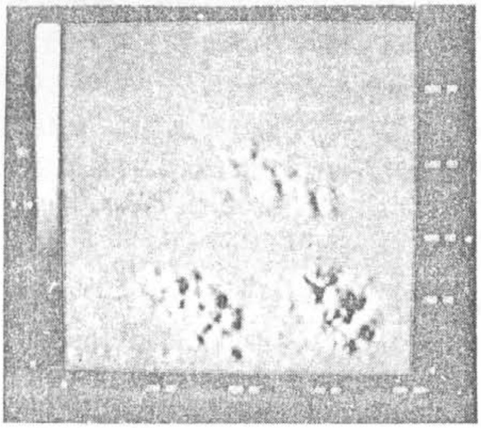


Fig. 1. Three similar structures indented on graphite surface consecutively at the three selected points and each structure included mounds and holes. Field size is 82×97 nm.

Figure 1 shows three structures produced consecutively at three selected sites and each structure included mounds and holes (scanning area 82×97 nm). The size and shape of the three structures were almost the same, indicating that the shape of the tip played an important role in forming nanometer structures.

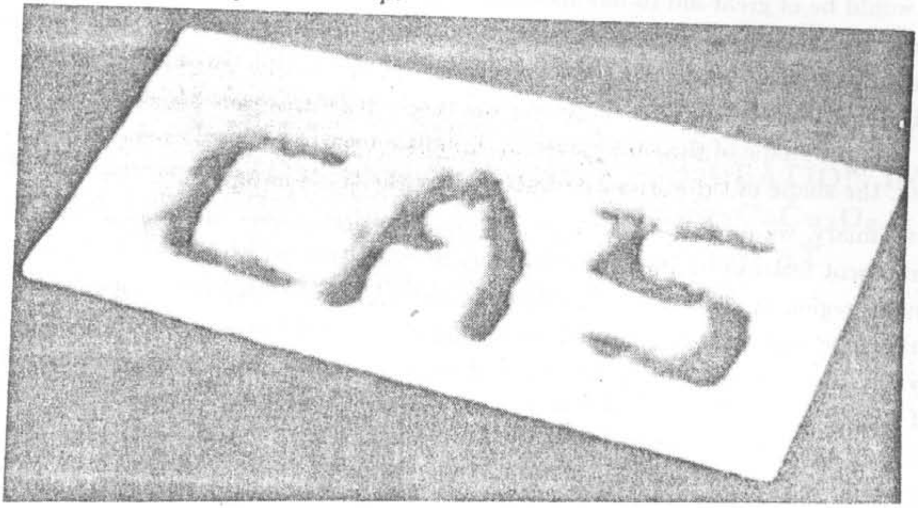
Figure 2 shows some characters written on graphite with line widths 10 nm controlled by a computer. The English characters "CAS" (abbreviation of Chinese Academy of Sciences) is displayed in Fig. 2(a), with individual letters 60 nm in size. It seemed to demonstrate that the process was due to the removal of one or more layer of graphite over a small area directly below the tip, but also a chemical reaction induced by the pulse might be responsible for structure formation. Figure 2(b) represents the English characters "CAS" caused by multiple-tip effect while modifying the surface, with the same condition as that in Fig. 2(a).

Operation of the STM (Ref. 2) is based on tunneling electrons due to an applied bias voltage between a conductive sample and a sharp metal tip separated by a few nanometers. So a strong electric field (could reach to 10^{-8} V/m) existing at the junction between the tip and the sample. While mapping the surface, a single atom at the apex of the tip contributed to imaging, because the tunnel density for free electron tunneling through a planar barrier with an applied voltage less than the work function of either the probe tip or the sample is given by

$$J = \frac{e^2}{h}\frac{k}{2\pi s} V \exp(-2ks) , \tag{1}$$

where s is the effective tunneling distance, k is the inverse decay length of the wave function density outside the surface, V is the bias voltage, e is the electron charge, h is Planck's constant, and $2k = 1.025\phi^{1/2}$. The effective barrier height ϕ is to a first-order approximation, the average of the probe tip and sample work functions.

Based on the operation of the STM mentioned above, it is concluded that the tunneling current is extremely sensitive to the tunneling distance between the tip and the surface. The tunneling current is confined to a filament between the apex of the tip and the surface or object under investigation. The tunneling current decreases by roughly an order of magnitude for every distance increase by 1 A, and the effective diameter of the filament $L_{\rm eff}$ can become extremely small for a pointed tip. In the case of a single atom at the apex, $L_{\rm eff}$ decreases to a magnitude of atomic dimension. While imaging the surface, the tunneling current is contributed mainly from the single atom at the apex of the tip.



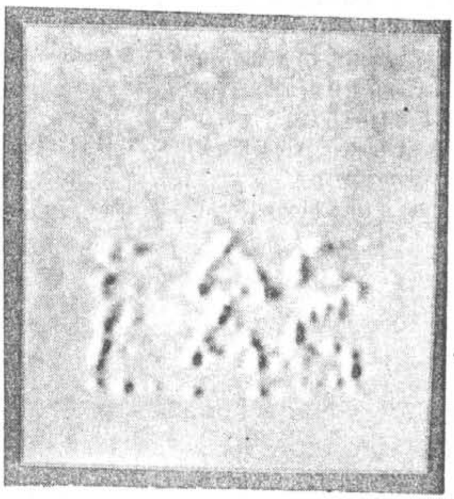


Fig. 2. The English characters "CAS" with individual letters 60 nm in size were written on graphite with line widths 10 nm. (a) Scanning area is 350×160 nm. (b) Multiple-tip effect while modifying the surface is met, scanning area is 414×487 nm.

On the other hand, while modifying the surface, the strong electric field existing between the tip and the surface plays a dominant role. However the electric field is inversely proportional to the distance between the tip and the surface. It is given by

$$E = \frac{V}{s}\,, \tag{2}$$

where V and s are the values the same as that in Eq. (1). So the nm scale region at the apex of the tip would be of great aid to modification. The probe tip which seemed to be very sharp on a macro scale would have some protrudent micro-tips. In the process of modifying the surface, the protrudent micro-tips would act on etching. Herein, multiple-tip effect was met. From the image in Fig.1, the size and the shape of the three structures were almost the same, indicating as well that the shape of the tip played an important part in forming nanometer structures. So to speak, the shape of the structure indented by the tip is in agreement with that of the tip.

In summary, we present a technique applying voltage across the tunnel junction for writing permanent features on graphite with lines about 10 nm width using our home-built STM. Nanometer region at the apex of the tip acts on etching. Multiple-tip effects while modifying the surface are explained in terms of the strong electric field existing at the junction between the tip and the surface. The shape of the structure indented by the tip is in agreement with that of the tip.

REFERENCES

[1] G. Binnig and H. Rohrer. Helv. Phys. Acta. 55 (1982) 726.
[2] G. Binnig and H. Rohrer. IBM J. Res. Develop. 30 (1986) 355.
[3] Z. H. Wang, C. C. Dai, H. Sun and C. L. Bai. Chinese Science Bulletin. 38 (1993) 433.
[4] T. R. Albrecht, M. M. Dovek, M. D. Kirk, C. A. Lang and C. F. Quate. Appl. Phys. Lett. 55 (1989) 1727.
[5] H. J Mamin *et al.*, J. Vac. Sci. Technol. B 9 (1991) 1398.
[6] J. Hu *et al.*, Jpn. J. Appl. Phys. 31 (1992) 110.
[7] J. L. Huang, Y. E. Sung and C. M. Lieber. Appl. Phys. Lett. 61 (1992) 1528.
[8] T. T. Tsong. Phys. Rev. B 44 (1991) 13703.
[9] C. L. Bai. Chinese Science Bulletin (in Chinese) 34 (1989) 339.