Nanometer-scale pit formation by scanning tunneling microscopy on graphite surface and tip current measurements

著者	羽根　一博
journal or publication title	Journal of applied physics
volume	75
number	2
page range	1228-1230
year	1994
URL	http://hdl.handle.net/10097/35570

doi: 10.1063/1.356462

Nanometer-scale pit formation by scanning tunneling microscopy on graphite surface and tip current measurements

Tsukasa Abe
Department of Electronic-Mechanical Engineering, Nagoya University, Nagoya 464-01, Japan
Kazuhiro Hane and Shigeru Okuma
Department of Electrical Engineering and Electronics, Nagoya University, Nagoya 464-01, Japan

(Received 19 May 1993; accepted for publication 13 October 1993)

Nanometer-scale pit formation by the application of pulse voltage was performed on highly oriented graphite in air with the simultaneous measurement of tip current. The tip current was measured to be on the order of microamperes. Regardless of the high current, the pit was not formed at pulse voltages less than a critical value. It is confirmed by the quantitative measurement of the current that high current is less important for pit formation under experimental conditions. The measurement of the critical voltage as a function of the tunnel resistance suggested the significance of high electric field for pit formation.

Nanometer-scale features have been generated on surfaces of several conductive materials using scanning tunneling microscopy (STM).[1] The STM lithographic process reported to date involves the formation of pits a few nanometers in diameter on a highly oriented pyrolytic graphite (HOPG) surface.[2–4] Hundreds of uniform pits were successfully generated by applying the pulse voltage between the tip and HOPG surface.[2] Monolayer cutting of HOPG was demonstrated by creating pits along the circumference of a circle.[5] The reproducible control over the pit diameter and a well-defined threshold voltage were obtained in aqueous solutions.[6] The graphite surface was etched reactively under octylcyanobiphenyl ambient in air.[7] More recently, it was reported that a polymer coating inserted between the tip and HOPG surface increased the probability of fabricating nanometer scale pits.[8]

From the mechanistic investigations performed on HOPG surfaces covered with pure water or other organic liquids, the requirement of the H_2O molecule for modification has been reported.[2,5,6] More recently, it was pointed out that the role of moisture in pit formation on the HOPG surface was physical as well as chemical in nature.[8] On the other hand, the mechanism for a similar nanometer-scale modification on noble metal surfaces was mainly attributed to field evaporation. At present, the mechanism of pit formation on the HOPG surface is not entirely clear. The chemical reactions[5] between graphite carbon and water molecules by current heating are possible processes involved in pit formation. Although the surface temperature rise caused by the modification process is calculated by assuming the tip current,[9] there are few reports on the quantitative measurement of the tip current.

In this work, nanometer-scale pits were formed by the application of pulse voltage on a HOPG surface in a humid environment with the quantitative measurement of tip current. The tip current and threshold voltage for pit formation were investigated at different tunnel resistances. The mechanism of pit formation on the HOPG surface is discussed with respect to the tip current.

A STM system was fabricated for the experiments. The tripod piezoelectric (PZT) scanner (50 nm/V) was used. The hysteresis of the PZT was minimized by inserting a capacitor.[10] The STM system was placed in an atmospheric environment. The current-voltage transforming amplifier (I/V converter) in the STM was constructed to measure the tip current in the range from 0.1 nA to 10 μA. The I/V converter consisted of two amplifiers (OPA128 and OPA111) connected in series. The values of gain of the two amplifiers were set to be 120 dB (OPA128) and 40 dB (OPA111) through use of feedback resistors of 1 MΩ and 100 kΩ, respectively. The total gain of the I/V converter was high enough to obtain an atomic image of the HOPG surface. The current flowing to the tip was measured by monitoring the output signal from the first amplifier (OPA128). The tips were fabricated by etching a tungsten wire (300 μm diameter) electrochemically in a solution of KOH (4%). The radius of the tip apex was evaluated by the scanning electron microscope to be approximately 100 nm.

Samples used in the experiment were HOPG (Union Carbide) freshly cleaved in air. The experiments were carried out in air under atmospheric conditions. A short square positive voltage pulse was applied to the sample for the surface modification. The tip was earthed through the input impedance of the I/V converter (approximately 10 Ω). The amplitude V_p of the square voltage pulse was from 2 to 4.4 V and the pulse duration was 110 μs. The voltage reduction by the input impedance during the modification was less than 100 μV. The voltage pulse was superimposed on a constant dc bias voltage (V_B, sample positive), which was used to image the surface in the constant-current mode. The total voltage applied to the sample was equal to V_p+V_B during pulsing. The bias voltage V_B was set equal to 0.5 V and the tunneling currents I_t were selected to be 0.1, 0.5, 2, and 10 nA to change the tip-to-sample distance before the application of the voltage pulse. The voltage pulses were generated with a computer (PC 9801 DX, NEC) and were applied through a digital-to-analog (D/A) converter (AZI-3301, Interface). When the voltage pulse was applied, the STM tip was retracted due to the

0021-8979/94/75(2)/1228/3/$6.00

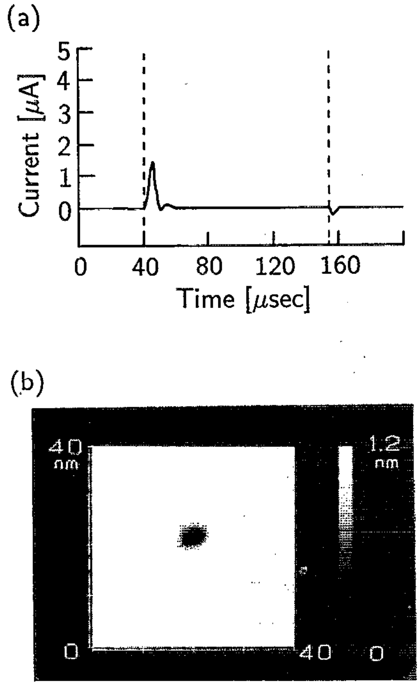

FIG. 1. (a) Current measured as a function of time. The pulse voltage is equal to 4 V and the starting and ending points of the voltage pulse are shown by the dotted lines. (b) Image of the pit formed after the application of the voltage pulse.

feedback control in constant-current mode. Since the speed of the tip retraction was 7 nm/ms, the displacement of the tip was equal to 0.8 nm during the application of a 110 μs pulse. The reduction speed was obtained from the change of the output voltage of the feedback circuit, which was applied to the PZT scanner.

Figure 1(a) shows an example of the current due to the application of the voltage pulse (V_p=4 V), and Fig. 1(b) shows the image of the pit fabricated on the HOPG surface (V_B=0.5 V, I_t=0.5 nA). As shown in Fig. 1(b), a circular pit of 8 nm in diameter and 1 nm in depth is produced. The current flow at the beginning of the voltage pulse is shown in Fig. 1(a). In this case, the maximum value of the current is equal to 1.5 μA and the width of the current pulse is approximately 8.2 μs. In our STM, when voltage pulse was applied, the current I_c induced by the instrumental capacitance (between tip holder and sample holder) was always observed. In Fig. 1(a), the current I_c(negative) is shown at the end of the voltage pulse. The current I_c(positive) having the same magnitude is superimposed on the measured tip current. The magnitude of I_c is 0.24 μA in Fig. 1(a). Since the value of I_c is approximately 16% of the maximum current, the current I_c has little influence on the feedback motion.

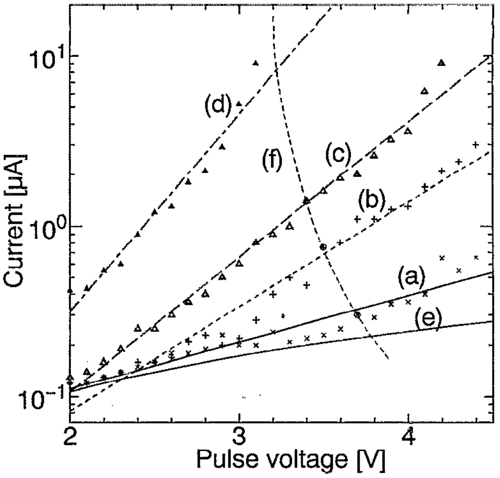

FIG. 2. Peak current measured as a function of pulse voltage at (a) I_t=0.1 nA, (b) I_t=0.5 nA, (c) I_t=0.2 nA, (d) I_t=10 nA, with (e) the current I_c induced by the instrumental capacitance and (f) the threshold voltage V_{th} for pit formation.

The currents measured under several conditions of I_t and V_p are summarized in Fig. 2. In Fig. 2, curve (e) shows the current I_c induced by the capacitance as a function of V_p and it increases linearly with the increase of V_p. Lines (a)–(d) in Fig. 2 show the peak values I_p of the tip current measured as a function of V_p for I_t of 0.1, 0.5, 2, and 10 nA, respectively. When the voltage pulse was applied, an abrupt increase of the current was sometimes observed at $V_p \sim 3$ V. We believed that this instability was caused by the conductive deposition on the sample or the tip.[6] We neglected the abrupt increase in current, and then the repeated measurements of peak values of I_p were averaged. The scattering of the peak value of I_p was evaluated by the standard deviation of the measured values to be typically 31% of the averaged value. The peak values changed from tip to tip; however the averaged peak current showed the repeatable variation when the clean tip and sample were used. The measured I_p increases exponentially as a function of the pulse voltage as shown in Fig. 2. The current I_c is 6.7% of the total current I_p at I_t=2 nA and V_p=4 V. With increasing V_p, I_p increases faster than I_c. The influence of I_c on the measurement of I_p becomes smaller at a large value of V_p. When I_t is equal to 2 nA, I_p can be expressed approximately by the equation:

$$I_p = 2.8 \times 10^{-3} \exp(1.3 V_p) \quad (\mu\text{A}),$$

with V_p in V, under our experimental conditions. When the pulse voltage was lower than a critical value (threshold voltage V_{th}), the pit was not formed. The value of V_{th} was measured with variations in I_p. Measured V_{th} is shown on the respective lines of I_p in Fig. 2 [dotted curve (f)]. It is found that the pit is not formed at $V_p < V_{\text{th}}$ even if I_p is considerably high. For example, when I_t=0.1 nA, the pit is fabricated at V_p=3.7 V and the current I_p is 0.3 μA. On the other hand, when I_t=2 nA, the current I_p is much higher than 0.3 μA at 3 V; however, the pit is not formed at V_p lower than 3.4 V. Moreover, when I_t=10 nA, although the current I_p is as high as 10 μA, the pit is not formed. Therefore, pit formation cannot be determined by the current I_p. Although we investigated the relationship between the pit size and the current I_p, a distinct relationship could not be found.

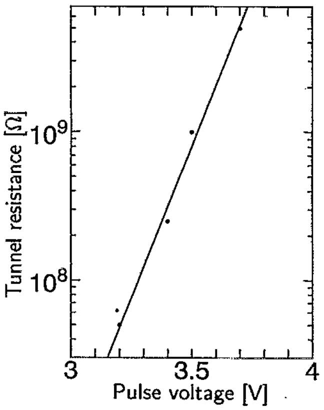

FIG. 3. Threshold voltage V_{th} measured as a function of tunnel resistance R $(=V_t/I_B)$.

The temperature rise ΔT at the surface after applying the voltage pulse was evaluated theoretically using Eq. (2) in Ref. 9; $\Delta T = Q/2\pi K\rho$, where Q, K, and ρ are heat source strength, thermal conductivity, and diameter of heat source, respectively. Under the conditions that $I_p=5$ μA and $V_p=4$ V, was calculated to be 20 μW. ΔT was evaluated to be about 2 K assuming that K of HOPG was uniform and equal to 1550 J/(m k) and ρ was 1 nm. It seemed that the temperature rise was too low for the pit to have been formed by the thermal effect of the current I_p.

The threshold voltage V_{th} for pit formation depended on I_t and V_B under our experimental conditions. The electric-field effect for pit formation was examined using the same method as that of Mamin, Guther, and Ruger,[11] and McBride and Wetsel.[12] In Fig. 3, measured V_{th} is plotted as a function of the tunnel resistance R $(R=V_B/I_t)$. It is noted that the value of R is obtained just before the pulse application and thus under the low-bias conditions. According to the simple model of metal-insulator-metal junction,[13] the tunnel current depends exponentially on the distance S between the metals. Therefore, ln R is linearly proportional to S. Although the tip moved at a constant retraction speed during the modification, the flowing current and electric field became maxima at the beginning of the pulse. Moreover, the size of the pit was not changed when the pulse duration was changed from 10 μS to 1 mS. Thus we believe that the surface modification occurred at the beginning of the pulse. As shown in Fig. 3, since V_{th} fit to a straight line, threshold electric field (dV_{th}/ds) is constant in the region of $R=10^7$–10^{10} Ω. This fact is direct experimental evidence that a threshold electric field is characteristic of pit formation on the HOPG surface. However, the role of high electric field in pit formation on the HOPG surface is still unclear since the H_2O molecule is necessary for the modification.[2,5,6]

In conclusion, the tip current flowing during the application of voltage pulse in nanometer-scale pit formation on the HOPG surface was measured quantitatively in air. The measured current was of the order on 1 μA, which was larger by three orders of magnitude than the tunnel current used for imaging. With increases in the pulse voltage, the peak current increased exponentially. However, the pit was not formed at pulse voltages less than a threshold value even with a current as high as 10 μA. The threshold voltage for pit formation depended linearly on the logarithm of the tunnel resistance. These results confirm that the current caused by the voltage pulse is less important and the effect related to the high electric field is responsible for pit formation on HOPG in air under our experimental conditions.

[1] R. H. Bernhard, G. C. McGonigal, R. Schneider, and D. J. Thomson, J. Vac. Sci. Technol. A **8**, 667 (1990).
[2] T. R. Albrecht, M. M. Dovek, M. D. Kirk, C. A. Lang, C. F. Quate, and D. P. E. Smith, Appl. Phys. Lett. **55**, 1727 (1989).
[3] J. A. Miller and R. J. Hocken, J. Appl. Phys. **68**, 905 (1990).
[4] K. Terashima, M. Kondoh, and T. Yoshida, J. Vac. Sci. Technol. A **8**, 581 (1990).
[5] W. Mizutani, J. Inukai, and M. Ono, Jpn. J. Appl. Phys. **29**, L815 (1990).
[6] R. M. Penner, M. J. Heben, N. S. Lewis, and C. F. Quate, Appl. Phys. Lett. **58**, 1389 (1991).
[7] J. P. Rabe, S. Buchholz, and A. M. Ritcey, J. Vac. Sci. Technol. A **8**, 679 (1990).
[8] S. L. Tang, A. J. McGhie, and M. E. Lewittes, Appl. Phys. Lett. **60**, 1821 (1992).
[9] P. F. Marella and R. F. Pease, Appl. Phys. Lett. **55**, 2366 (1989).
[10] H. Kaizuka and B. Sin, Jpn. J. Appl. Phys. **27**, 773 (1988).
[11] H. J. Mamin, P. H. Guther, and D. Ruger, Phys. Rev. Lett. **65**, 2418 (1990).
[12] S. E. McBride and G. C. Wetsel, Jr., Appl. Phys. Lett. **59**, 3056 (1991).
[13] J. G. Simmons, J. Appl. Phys. **34**, 2581 (1963).