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FABRICATION OF GOLD NANOSTRUCTURES ON GRAPHITE USING ATOMIC FORCE MICROSCOPE

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Abstract Various nanostructures are created on graphite in air through the field-induced deposition of gold atoms from the gold-coated tip of atomic force microscope (AFM). The nanolithography controlling system we developed makes it possible to fabricate arbitrary complicated patterns and to optimize the deposition conditions fast and easily. We found that gold mounds can only be created by tip-negative pulses within the pulsed voltage range of ± 20 V, 0.2 - 300 msec, and the size of gold mounds and the threshold voltages are highly dependent on the geometry of Au-coated tip. Our results support the mechanism of field evaporation of negative gold ions.

INTRODUCTION

Fabrication of nanometer-scale structures using scanning probe microscopes (SPMs) has generated great interests from both fundamental and technological points of view. Among various experimental approaches for such nanofabrication is the field-induced deposition of gold atoms from a gold STM tip or gold-coated AFM tip by applying voltage pulses to the tip. Since the first report by Mamin et al.,¹ lots of work have been done for the purpose of elucidating the deposition mechanism of gold and of creating reliable and stable gold patterns on different substrates.²⁻⁷ However, the mechanism is still the point at issue and a number of different mechanisms have been proposed to explain the experimental results, involving field evaporation,¹ mechanical contact,² and local heating.³⁻⁴ In this paper, we report our results of gold deposition on graphite surface. With the use of the novel nanolithography controller we developed, we could be able to *print* arbitrary complicated gold patterns on graphite with nice reliability. The results we got also shed some light on the deposition mechanism.

EXPERIMENTAL SECTION

A Nanoscope III AFM from Digital Instruments(DI, USA) was used for the field-induced evaporation of gold in air. A PC-486 computer with a DAS 1601 DA/AD board (Keithley, USA) was incorporated into the AFM to control the lithography process. The Au-coated AFM tip was prepared by sputtering 100nm gold on a silicon cantilever(DI). Highly oriented pyrolytic graphite(HOPG) was used as the deposition substrate. The encoded patterning voltage pulses were applied to the Au-coated AFM tip to regulate the electric field between tip and substrate. A constant repulsive force was used for both gold deposition and AFM imaging. A Hokuto Denko HA-150 potentiostat (Tokyo, Japan) was employed to perform the AFM-based I-V measurement,⁸ in which a resistor (several megaohms) was inserted into the circuit in series with the tip for limiting the current below 10 μ A.

RESULTS AND DISCUSSION

Only mounds were observed on graphite surface by applying voltage pulses to the gold-coated silicon tip. The formation of mounds seems to be polarity dependent and they were only created by applying negative voltage pulses at least in the experimentally used pulse ranges of -20V ~ +20V in amplitude and 0.2msec ~ 300msec in width. Figure 1 shows the typical results we got, where (a) is the dots array of gold obtained with pulses of -10V for 1msec and (b) is the logo of Peking University *printed* on HOPG using the same pulses.

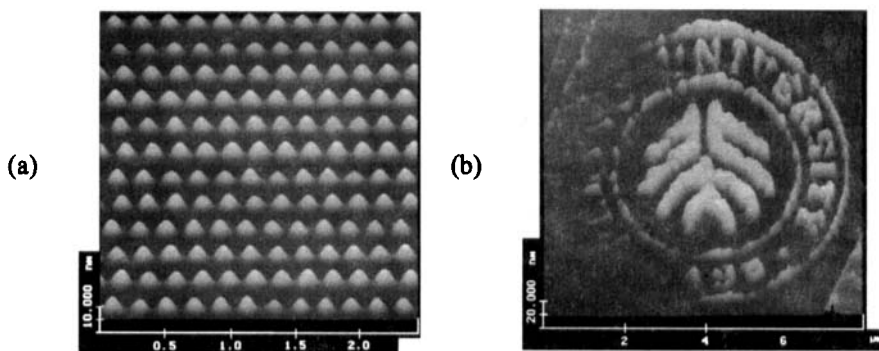


FIGURE 1. (a) Array of gold mounds on HOPG made with pulses of -10V for 1 msec; (b) Logo of Peking University *printed* on HOPG using the same voltage pulses as in (a). (See Color Plate I).

FABRICATION of AU NANOSTRUCTURES on HOPG USING AFM

The mounds are typically 70 nm across at half the height of the mounds and 4nm high.

The threshold voltage for mound creation was tip dependent, typically -5V for a well-coated silicon tip. Assuming the gap between tip and substrate is 0.5nm, then the threshold field is ca. -10V/nm, where the theoretical threshold field is 10.3V/nm for Au⁻ and 30.7V/nm for Au⁺ assuming the gap between the tip and substrate is 0.50 nm according to the model proposed by Tsong.⁷ The quality of gold-coated silicon tip was checked by two different ways: directly imaging by scanning electron microscope(SEM); or measuring the contact resistance between the AFM tip and the graphite substrate using our AFM-based I-V probing system.⁸ Usually a tip whose apex is well-coated with gold has a contact resistance as low as 3k Ω . After numerous repeated use of the same tip, the threshold voltage showed gradual increase. The SEM image shown in Fig. 2(a) indicates that the gold at the very end of the tip has been used up in this case. The contact resistance of such a used tip with HOPG was distinctly increased, even larger than 10¹¹ Ω . We also tried to deposit gold on graphite using such imperfect tips. In Figure 2(b) is given one of the representative results, in which multiple mounds were created by one single voltage pulse. We must also consider the possibility of multi tip effect, in fact, we did not observe multi tip effect in imaging 100 nm gold particles using the same tip.

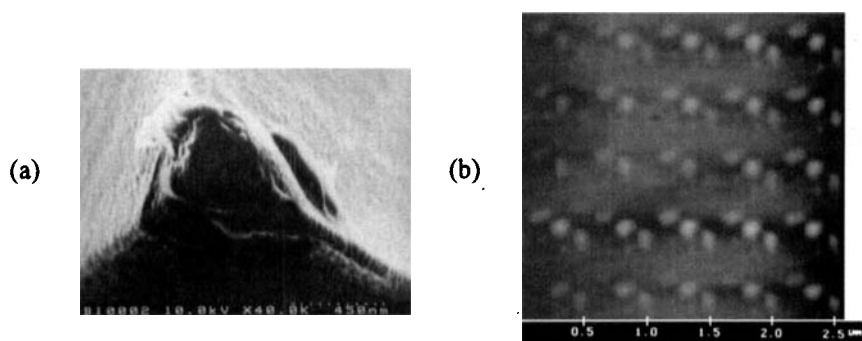


FIGURE 2. (a) SEM micrograph of a gold-coated silicon tip that has been repeatedly used;(b) Multiple mounds were created by one pulse. 5 x 5 voltage pulses of -10.0V and 0.19msec were applied to a used tip as shown in Fig 2(a) (See Color Plate II).

The above observations strongly support the field evaporation mechanism: under the ultrahigh electric field created by applying negative voltage pulse to the Au-coated tip, the gold atoms were negatively ionized and field-evaporated to the graphite surface.

threshold voltage. With a very high voltage pulse, simultaneous evaporation of gold located at highly-separated sites of the tip would occur, leading to the formation of multiple mounds.

The polarity-dependence and the following results may be used to exclude the contact mechanism. When performing the contact resistance measurement of the Au-coated tip, the tip was made contact with the graphite surface and the I-V characteristic was recorded, we never found the formation of gold mounds on the graphite surface as long as the applied voltage was not so high, indicating that contacting is not the prerequisite for mound formation. Recently, Hsiao et al deposited gold mounds on silicon surfaces by applying voltage pulses to a gold STM tip and confirmed by elemental analysis using the field emission scanning Auger microscope that only nanostructures formed via tip-negative bias pulses are metallic, although nanostructures produced with both polarities using the same tip are virtually indistinguishable in STM images of these features.⁵ In addition, the local heating mechanism may also be difficult to explain the multiple mounds formation: the Joule heat or the Nottingham effect would most possibly result in one mound rather than multiple mounds with a single voltage pulse.

In summary, we have successfully created gold nanostructures on graphite with high probability by using our AFM-based nanolithography system. The results we got strongly support the mechanism of field evaporation of negative gold ions.

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