Diamond-coated tips and their applications

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Scanning tunneling microscope (STM) has recently demonstrated its potential application as a powerful tool for nanometer-scale surface modification. We have successfully fabricated new types of diamond-coated STM tips by using microwave plasma chemical vapor deposition (MPCVD). The reactant is a gaseous mixture of methane and hydrogen, sometimes adding oxygen. While natural diamond is a good insulator, the electrical conductivity of diamond-coated tips made by MPCVD technique is always high enough for STM experiments. These tips are quite stable, hard enough to make machining on metal or other solid surfaces in nanometer scale. We have applied the diamond-coated STM tip to so-called controlled machining on the metallic surfaces, such as gold, silver, and platinum films, and even polycrystal platinum, single crystal nickel, and palladium. Further investigations, including the results caused by different tips, applications for nanometer-scale processing and engineering, etc., have been discussed. This technique might become a potential useful tool for nanometer science and technology in the future.

I. INTRODUCTION

Since the scanning tunneling microscope (STM) has developed rapidly as a method for working on the nanometer scale,[1] manufacturing of STM tips with special physical or chemical properties and even special shapes becomes more and more important. Such tips must not only get stable high resolution images under normal operating conditions but must also perform different kinds of processing on nanoobjects under sometimes critical conditions such as mechanical machining on solid surface, etc. The most commonly used STM tips are made of tungsten (W) by electrochemical etching or platinum–iridium (Pt–Ir) by mechanical cutting. However, the conventional tips are often fragile, and can easily become deformed or damaged when they come in contact with the sample surface during surface modification. Diamond has attracted more attention due to its extreme hardness and chemical inertness. Based on the above suggestions, it is reasonable to combine the conventional tip and diamond together to fabricate a novel diamond tip. Kaneko *et al.*[2] and Visser *et al.*[3] have used diamond to manufacture polished semiconducting STM tips. Germann *et al.*[4] have also prepared single crystal diamond on AFM tips by chemical vapor deposition (CVD), and we have made a different kind of diamond-coated STM tip by microwave plasma chemical vapor deposition (MPCVD) for the first time.[5]

For STM or scanning force microscope (SFM), the mechanical surface machining was mostly done on soft materials such as organic films[6–10] and gold films.[5,10] Because diamond has the highest hardness in all materials, the diamond-coated STM tip has great potential to expand the field of nanomachining to an unprecedented realm. In the experiments, we first used diamond-coated tips to do nanometer controlled machining not only on gold, silver, and platinum films but also on the surfaces of harder bulk samples of polycrystal platinum, single crystal nickel, and palladium. The present article gives results that clearly demonstrate the hardness of our diamond-coated tips. This technique might become a useful tool for nanometer science and technology in the future.

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II. EXPERIMENTS

A. Diamond-coated tips preparation

Tungsten tips are made from 0.2-mm-diameter tungsten wire, and a desired tip shape is created by conventional electrochemical etching in a 2-mol/ℓ aqueous NaOH solution. The radii of the tips are less than 100 nm. After etching, tips are treated in an ultrasonic bath with diamond powder to generate fine scratches, which would serve as the nucleation sites. Then, some treated tips are put on a silica glass plate and placed in the tube to fabricate diamond-coated tips by MPCVD. The reactant is a gaseous mixture of methane and hydrogen, and sometimes oxygen is added. The detail of the process is reported elsewhere.[11]

B. Surface modification by the diamond-coated tips

A domestic STM setup (CSTM-9100, manufactured by the Institute of Chemistry, Chinese Academy of Sciences) was employed to do surface modification at nonometer scale. In the experiments, the diamond-coated tips were used as both scanning probe and machining tool. Before the machining, the objective surface was imaged by using the diamond-coated tip under normal scanning conditions (I_t<1.0 nA, $V_{bias}\sim$ hundreds mV, about 1 image/min.). Then we raised the tunneling current to 6–10 nA and lowered the bias voltage to <100 mV. The feedback circuit of the STM electronic controller was damped and the diamond-coated tip was introduced to scan an area in the constant height mode for 5 or 6 times within 30 s. After the controlled machining process, we reset our STM to normal scanning conditions and imaged the surface including the machining area using the same diamond-coated tip.

As a supplemental experiment, the modification on the highly oriented pyrolytic graphite (HOPG) surface with diamond-coated tip was done by using the voltage pulse dur-

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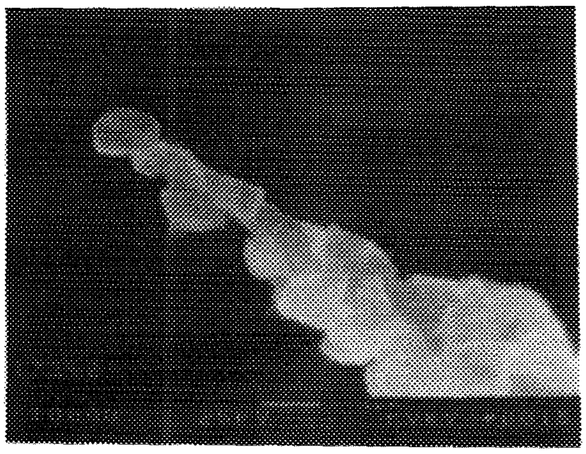

FIG. 1. SEM image of a typical diamond-coated tip fabricated by MPCVD method.

ing scanning. The result was compared with that caused by using a normal tungsten tip to further reveal the mechanism of voltage pulse modification.

III. RESULTS AND DISCUSSIONS

The diamond-coated STM tips are observed by using a scanning electron microscope (KYKY-1000B, manufactured by Beijing Research and Development Centre of Scientific Instruments, Chinese Academy of Sciences). Figure 1 shows the shape of a typical diamond-coated tip made by MPCVD. It can be found that on the top of the tip, a certain corner of a diamond grain replaces the role of original W apex. On the other hand, while natural diamond is a good insulator, it was found that the electrical conductivity of diamond-coated tips made by MPCVD is always high enough for STM experiments. This conductivity under STM conditions also appeared in the case of diamond films made by MPCVD.[12,13] It is possibly due to impurities and hydrogenation induced during MPCVD.[14-16]

In the experiments for nanometer scale controlled machining, we employed the diamond-coated tips not only on various metallic films but also on surfaces of much harder bulk sample of single crystal and polycrystal metals.

To demonstrate the hardness of the diamond-coated tips, we selected gold, silver, and platinum films and fine prepolished bulk sample surfaces of polycrystal platinum, single crystal nickel, and palladium as the machining objects. We give the results and further discussions in the following.

A. Machining on Au, Ag, and Pt films

The films of gold, silver, and platinum were prepared on mica by physical vapor deposition (PVD) in a vacuum chamber. The resultant grain size measured by STM varies from about 10 to 30 nm. A typical result of mechanical machining on gold film is shown in Fig. 2. Sometimes we observed that the surface structure of the areas to the left and right of the machining area had been disrupted, and the grains looked like they had been pushed and squeezed. But after a time, these areas were restored to the normal structure as those of undisrupted areas. Based on these results, we believe that the

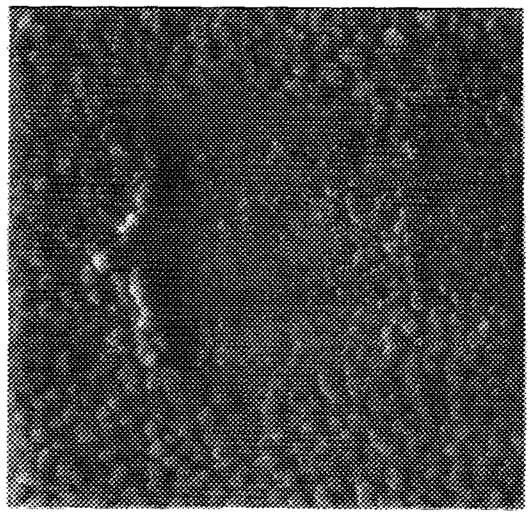

FIG. 2. A 700 × 700 nm scan (I_t=0.90 nA, V_{bias}=453 mV, sample positive) of gold film prepared by PVD after a controlled machining. The grain size is about 20 nm. The machining area shows a much smoother surface not having the original cumulated grain structure.

machining effect is mainly due to mechanical planing in which the diamond-coated tip acts as the plane to cut off the topmost layer of gold film. The machining area has much less undulation than the areas without machining around it, and it shows a quite flat surface without the cumulated grain structure of the original gold film. Since there are hardly any hints of where the cutoff part goes, and sometimes after machining the quality of the image may change suddenly several times, we believe some gold grains cut off from the film adhered to the tip. This is possible because the gold film has quite a loose structure, and binding among the gold grains is rather weak. So it is easy to cut them off and remove them by the tip.

In the cases of silver and platinum films, the machining effects are quite similar to that of the gold film. The only difference is that silver films have a higher hardness than gold films, and platinum films are even harder. Thus we must use a higher tunneling current, i.e., we must put the tip even closer to the sample to make machining possible.

B. Machining on the surfaces of polycrystal Pt, single crystal Ni, and Pd

In order to reveal more of the mechanism of the machining process, we tried machining on harder samples. Since normal metals have too rough a surface at nanometer scale and they are easy to oxidize in air, we selected fine-polished surfaces of polycrystal platinum and single crystal nickel and palladium as the machining objects.

Figure 3 shows the machining area on the surface of polycrystal platinum which somewhat reveals a machining effect. We believe this effect is mainly due to mechanical planing in which the diamond-coated tip acts as a plane to cut off the topmost layer of the sample. Although there may be also some other effects such as heating of the sample by high tunneling current and electrical field induced material transmission between tip and sample contributing in machining,

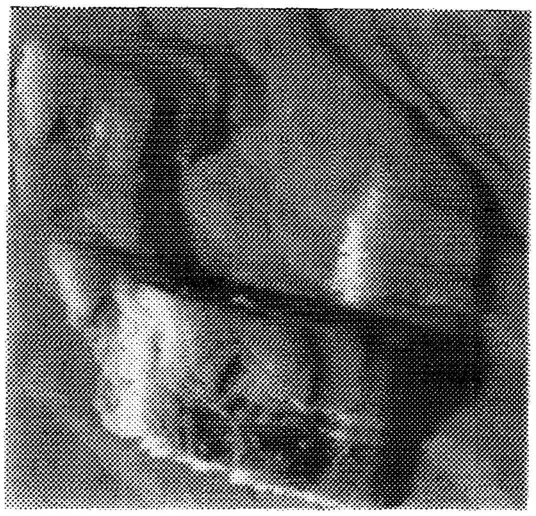

FIG. 3. A 550 × 550 nm scan (I_t=0.60 nA, V_{bias}=59 mV, sample positive) of bulk sample surface of polycrystal platinum produced by diamond-coated tip. The machining area inclines a little to the bottom right due to the thermal drift during the machining. Materials were piled up to the left, right, and bottom sides of this area. There was no such pileup to the top right side because the sample surface sloped from the bottom left to the top right.

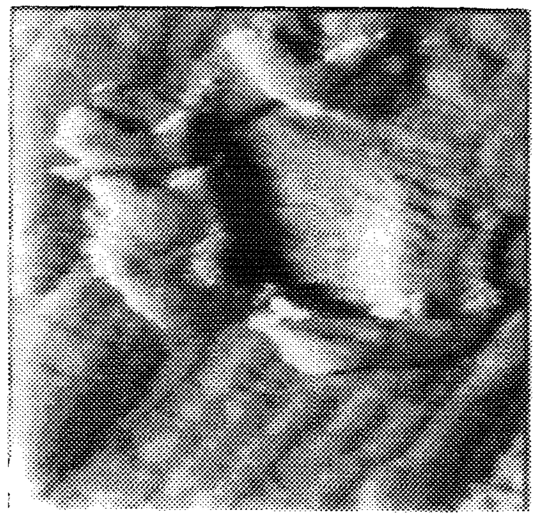

FIG. 4. A 600 × 600 nm scan (I_t=0.60 nA, V_{bias}=60 mV, sample positive) on a (100) surface of nickel after machining. Materials were piled up to almost every side of the machining area since the sample surface sloped only a little this time.

we can see clearly from the picture that these effects are not the prominent ones. The machining area inclines a little to the bottom right because of the thermal drift of the sample during the machining. Dramatically different from the case of films, the machining area was surrounded by piled up materials with a layered structure in the left, right, and bottom side. We believe this is firm evidence that the main effect of our machining process is mechanical planing. The hard diamond-coated tip cut into the sample during the machining, and at each scan of the area it planed up one layer of material of the sample and pushed it to the side. Because the sample bulk has such a compact and homogeneous structure, the layer planed up from the surface still connects to the sample at the edge of the machined area. Instead of being adhered and moved to other places by the tip, these materials were piled up layer by layer at the side of the machined area. There is no such pile up to the top right side of the machined area. This may be due to the fact that the sample slopes from bottom left to top right. In the case of constant high mode, the diamond-coated tip cannot cut off the surface of the top right part.

The results of nanometer scale mechanical machining on single crystal nickel and palladium are quite similar to that on the polycrystal platinum. Figures 4 and 5 show the results of machining on the (100) surface of single crystal nickel and the (111) surface of single crystal palladium, respectively. The surface structure of the samples and the results of the machining are comparable to that which we described in the case of polycrystal platinum. Actually, the polycrystal and the single crystal samples are no different at nanometer scale because the size of the crystalline grain in a polycrystal is in the order of a micron.

Before and after the controlled machining process, the quality of the images got by the same diamond-coated tip has no obvious change. An important phenomenon is that two consecutive machinings always get results very similar in detail. This confirms that no major change occurred to the diamond-coated tip during the controlled machining process. Thus the hardness of our diamond-coated tip is prominent. Another conclusion to be drawn is that the piled up materials seen in the cases of bulk samples cannot be the parts of the tip fallen down.

Comparing the machining effects between film and bulk samples, it is found that no obvious piled up material has been observed in the case of the films. This is possibly because the structure of such films is quite loose and binding among the grains is rather weak. So it may be easy for the grains to be cut off from the sample and then migrated easily to other places.

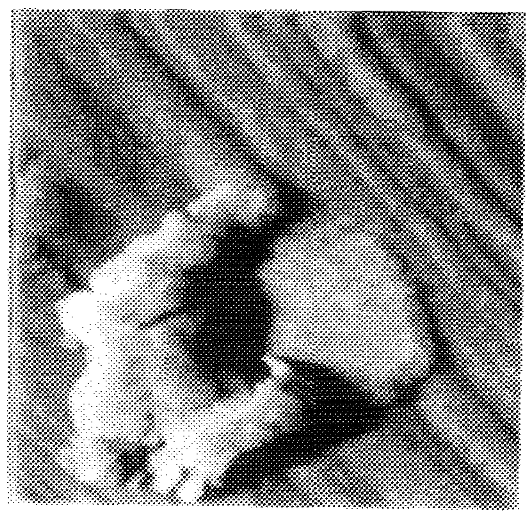

FIG. 5. A 800 × 800 nm scan (I_t=0.60 nA, V_{bias}=60 mV, sample positive) on a (111) surface of palladium after machining. Materials were piled up to the left and bottom sides of the machining area because the sample sloped from the bottom left to the top right.

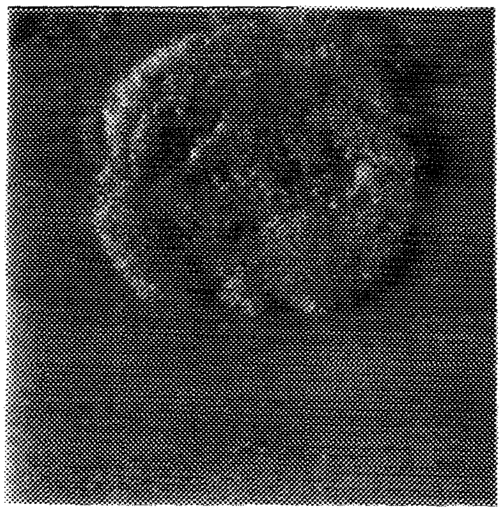

FIG. 6. A 175 × 175 nm STM image produced by a diamond-coated tip with voltage pulse (constant current mode, $I_t = 1.24$ nA, $V_{bias} = -189$ mV; pulse: 50 μs/+6 V).

C. Voltage pulse effects during scanning on the HOPG surface

We applied a voltage pulse on the tip during scanning on the HOPG surface. The results showed there were different effects for the normal tungsten tip and the diamond-coated tip. In the case of the tungsten tip, there are some alternative holes and hillocks on the HOPG surface. Otherwise, in the case of the diamond-coated tip, as shown in Fig. 6, a relatively large "pie" shape appeared on the HOPG surface; perhaps this was caused by emission carbon contamination of the diamond-coated tip which was not terminated with hydrogen plasma. Because in the rich H atmosphere the diamond surfaces are believed to be terminated with hydrogen,[17] they have a low surface energy and should become contaminated less than those surfaces that are not terminated by hydrogen.

IV. CONCLUSIONS

Based on above discussions, we have successfully fabricated new kinds of diamond-coated tips by MPCVD. With these diamond-coated tips, controlled machining on various metallic surfaces and voltage pulse modification on HOPG surface have been done. The experiments demonstrate the hardness of our diamond-coated tips by successfully doing nanometer scale mechanical machining. The above results are from our preliminary research. Further study, including the mechanism of surface modification, R&D of nanoprocessing and engineering, etc., have been carried out in our laboratory. MPCVD has great potential to become a powerful tool for nano science and technology.

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