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Microwave plasma chemical vapor deposited diamond tips for scanning tunneling microscopy

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Diamond microparticles were grown on etched tungsten wires using a microwave plasma-assisted chemical vapor deposition process. The apexes on cubo-octahedral particles bound by {100} and {111} facets were effectively used as tunneling tips for scanning tunneling microscopy. The atomically resolved surface image of highly oriented pyrolytic graphite was acquired. Tunneling characteristics revealed a higher electron emission from the diamond tips than that from the platinum–iridium tips. The same diamond tips were used to produce surface indentation and its image. © *1997 American Institute of Physics.* [S0003-6951(97)04045-X]

Surface images of atomic resolution are routinely obtained using scanning tunneling microscopy (STM) and atomic force microscopy techniques. Currently, various forms of these microscopic techniques, collectively known as scanning probe microscopy (SPM), are used in many scientific fields such as materials research, biological studies, high-density recording and readback, and nanofabrication and nanocharacterization of electronic devices.[1–4] The most delicate component in all these SPM techniques is the probe. STM probes are made of conducting materials, usually metals, for a good source of electrons; they have a high aspect ratio and a very small radius of curvature for the tip. The image resolution depends on the sharpness of the tip. Also, the tip should be chemically inert for stable operation. However, a metal tip is susceptible to mechanical damage, oxidation, and adsorption of impurities, all of which will change its tunneling properties. Its radius increases due to tip wear, which alters the electric field around it leading to changes in the operating parameters and loss of resolution Because of these problems, a metal tip is not durable and reliable for continuous image acquisition or nanomanipulation.

Among the many unique properties of diamond, its high hardness and low coefficient of friction are most suitable for its use as a tip material. Another interesting property of diamond is the negative electron affinity (NEA), which reduces the potential barrier for electron emission.[5] The work function measured using a field-emission retarding potential has been found to be 4.15 eV, which is lower than the diamond band gap,[6] an essential condition for NEA. For applied negative bias, enhanced electron emission was observed due to both Fowler–Nordheim tunneling and NEA. Electron emission from undoped diamond films has been obtained at fields as low as 2×10^4 V/cm.[7,8] For a given voltage, the electric field in diamond can be enhanced further if it is made in the form of a tip.[9] Diamond tips have several advantages over metal tips. Being the hardest material, it is robust against erosion due to high electron current flow. The diamond surface does not favor any strong bonding of gases such as oxygen and nitrogen; hence, the electron emission properties will be unaffected in the presence of these gases in the operating environment. Moreover, a solid oxide does not build up on the diamond tip, and strongly bonding gases such as hydrogen and fluorine are believed to enhance the electron emission from diamond. Since diamond tips emit electrons at a low field, the field-induced damage of diamond tips will be further reduced. It is anticipated that a diamond tip may overcome the problems associated with metal tips while maintaining constant and reliable tunneling properties.

For STM applications, a method has been described to polish and shape a piece of bulk diamond as a tip and implant it with boron ions to increase its electrical conductivity.[10] This method is prohibitively expensive. Similarly, a conducting diamond layer has been grown homoepitaxially on an insulating bulk diamond using boron doping.[11] The sample was then polished to get a sharp tip on the grown film so that tunneling occurred from the conducting diamond tip. In both cases, the shaped diamond tips were attached to a metal electrode by brazing or by other means. Attempts have also been made to make diamond tips on chemically etched tungsten probes.[12,13] The grown diamond was larger than the metal tip and did not produce a well-defined tip configuration. Similarly, a silicon tip was coated with a 120 nm thick diamond film that was doped with boron in the gas phase to increase its conductivity.[14,15] In this letter, we report

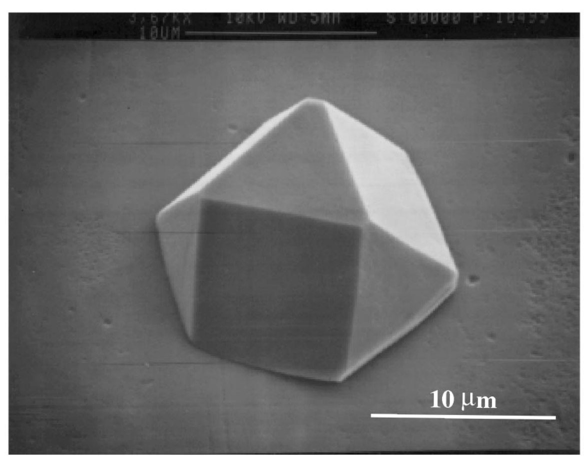

FIG. 1. A SEM of a single diamond cubo-octahedral microparticle grown on a tungsten substrate. The octahedron side is approximately 7.5 μm. Note the three apexes bound by {100} and {111}.

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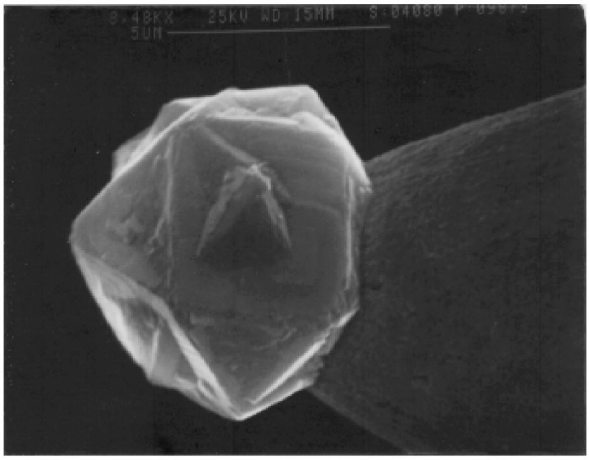

FIG. 2. SEM picture of a diamond particle grown on a tungsten tip. Note that the apex of the diamond tip is along the axis of the tungsten probe.

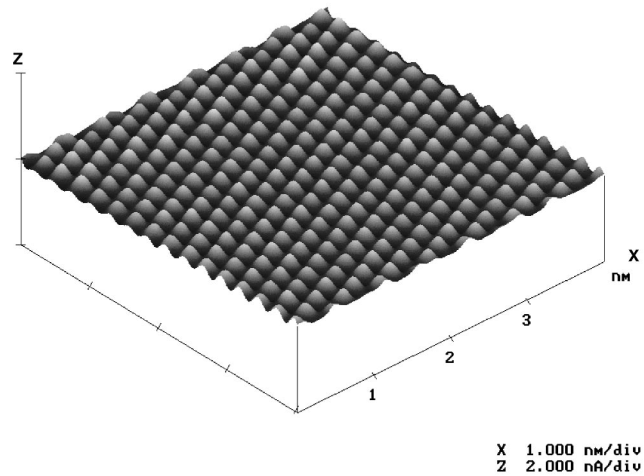

FIG. 4. Surface image of HOPG obtained using a diamond tip under constant height mode.

the results of our investigation to fabricate chemical vapor deposited (CVD) diamond tips on tungsten and demonstrate their application for high-resolution STM imaging.

A microwave CVD system (AsTex) with automatic pressure, temperature, and gas flow controllers was used to grow diamond. Diamond microparticles were grown using a gas mixture of 1% CH_4 in H_2. The pressure, susceptor temperature, and microwave power were optimized to grow diamond particles with well-defined facets. Figure 1 shows a scanning electron microscope (SEM) photograph of a single microparticle grown on a tungsten plate at 900 °C using 1 kW of microwave power and 60 Torr gas pressure. The diamond particle has a cubo-octahedral shape with a cube side of approximately 7.5 μm. Three apexes bound by {100} and {111} planes can be seen around the top {111} surface. If this crystal is grown on a metal probe such that it is oriented properly with one of the apexes along the axis of the metal probe, it could function as a STM tip. Such a tip would have an aspect ratio close to unity. An electrical contact could automatically be established between the metal probe and the diamond particle, unlike the bulk diamond tip samples requiring brazing or bonding. For the particle shown in Fig. 1, the apexes have grown beyond the condition for the sharpest point and the crystal is too large for STM imaging application. By controlling the growth time, a sharp diamond tip matched with the aspect ratio of the metal tip can be obtained. To validate this point, diamond growth on a sharp metal tip was attempted. Tungsten wires of 0.25 mm diameter were etched and polished electrolytically. Selective nucleation was carried out prior to diamond growth. The tungsten tip was pressed against a surface coated with diamond paste containing 0.1 μm diamond particles. It was experimentally found that a force of approximately 7×10^{-4} N was sufficient to nucleate diamond particles during the growth process.

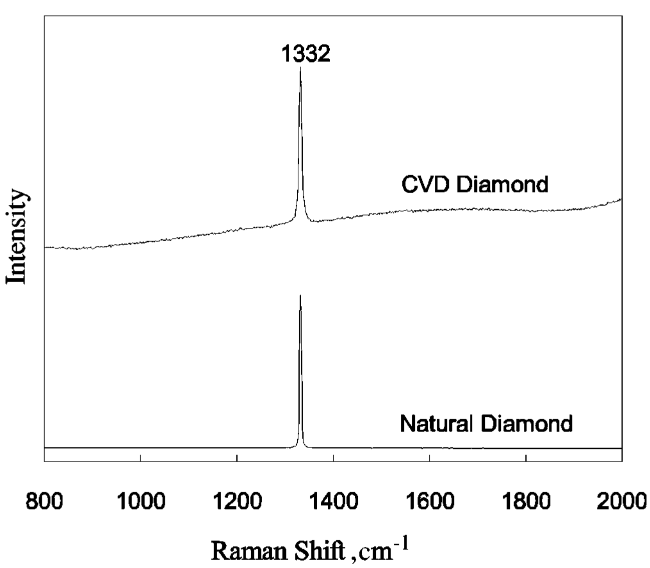

FIG. 3. Raman spectra of the CVD diamond particle and a natural bulk diamond.

Figure 2 shows a SEM picture of a diamond particle grown selectively on a tungsten tip. It clearly reveals the apexes bound by the {100} and {111} planes. The apex of the diamond tip is along the axis of the tungsten probe. The location of the nucleation site at the metal tip was found to be critical in producing diamond tips aligned along the axis of the metal tip. Under the process conditions given above, approximately 30% good tips were obtained for a typical growth run containing 40 tips. In Fig. 2, the cube side of the diamond particle is about 4 μm. A secondary growth is seen from the {100} facets, along ⟨100⟩ directions, producing {111} facets. Such a secondary growth direction is also observed in natural diamond. This result leads to two options

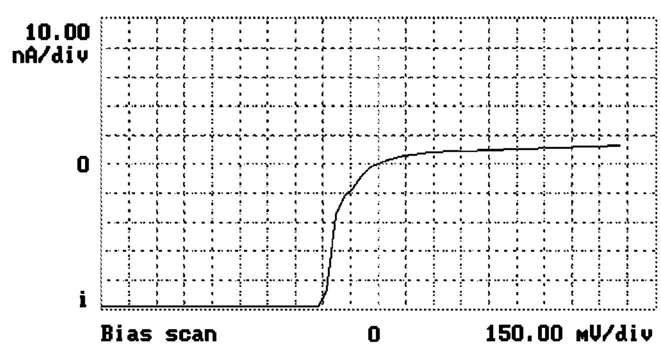

FIG. 5. Typical STM $I-V$ characteristics of the diamond tip obtained from a gold film sample in air.

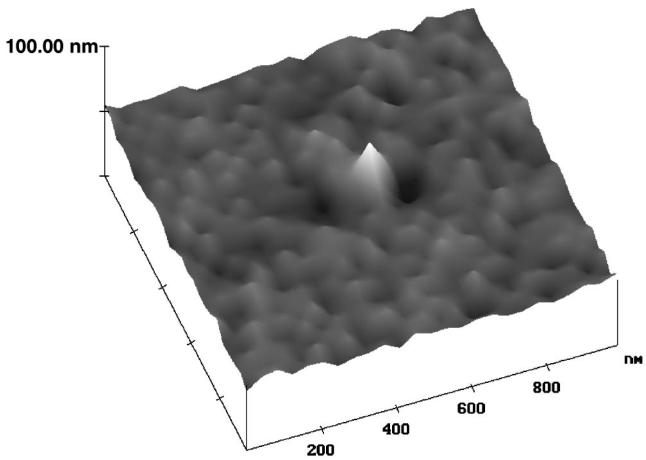

FIG. 6. Inverse image of an indentation produced and imaged by the same diamond tip.

for a diamond tip: we can use either the apexes formed by the {100} and {111} planes or the {111} pyramids formed by secondary growth on the {100} planes. However, the apexes or {111} pyramids must be along the axis of the metal probe. The tunneling results presented here are for the former.

In Fig. 3, we show the Raman spectrum of the CVD diamond particle shown in Fig. 2 along with that of a natural diamond. The Raman line is broader for the particle compared to that of natural diamond, but both have the same peak at 1332 cm^{-1} corresponding to sp^3 bonding. The quality of the particle is good, judging from the very weak features corresponding to graphitic carbon.

The diamond tip is used for STM imaging of highly oriented pyrolytic graphite (HOPG) using a Digital Instruments Nanoscope III. Figure 4 shows an atomically resolved surface image of HOPG in air under constant height operating conditions. The resolution is comparable to that obtained using a Pt–Ir tip. Figure 5 shows typical STM current–voltage ($I-V$) characteristics of a diamond tip acquired using a gold film sample. Though the diamond tip is undoped, it shows an asymmetrical $I-V$ curve giving more current for negative bias. For a given voltage, the current is higher than that obtained using a Pt–Ir tip from the same gold sample. The high current from the diamond tip may be due to a larger tip area, compared to that of the Pt–Ir tip. Since atomic resolution is attainable, we believe the diamond tip area is comparable to the Pt–Ir tip area. Therefore, the enhanced electron emission may be partially due to NEA, though this is not independently verified in our experiment. We have not measured the radius of the diamond tip in this experiment, but the shape of the tip is reproduced by indentation in the gold film deposited on a silicon sample, and imaged by the same diamond tip. The inverse image in Fig. 6 shows clearly the impression of the diamond facets leading to a tip. The indentation was conducted repeatedly and the diamond tips were found to be durable, though further systematic study is warranted. Research is in progress to increase the aspect ratio of the diamond tip.

In conclusion, atomic resolution of STM image suggests that the CVD diamond tip is viable as a STM probe. Tunneling characteristics of undoped diamond tips show enhanced electron current. Micromorphological control is required to produce sharp diamond tips. Nanoscale manipulation can be conducted without damage to the tips.

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