

CVD diamond probes for nanotechnology

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Abstract. Diamond tips are attractive tools for nanoscience because of their hardness and, when doped chemical vapor deposited (CVD) diamond is used, their electrical conductivity. In this article, devices based on CVD diamond coated silicon tips and molded diamond pyramids are described. A new type of tip, with a controlled selectively deposited diamond coating, on its upper part only, is presented, which will be useful for integration with actuators, sensors, etc. Pyramidal diamond tips with cantilevers have been micromachined and characterized, with apex radii in the range 10 to 40 nm. Structuring the diamond layer by reactive ion etching resulted in a very well defined shape of the cantilever. From resonance frequency measurements, Young's modulus of the diamond cantilevers was found to be in agreement with reported values. Preliminary tests have shown the pyramidal tips to be suitable for atomic force microscopy.

Doped CVD diamond is useful for nanoprobe microscopy due to its hardness, high Young's modulus, electrical conductivity through doping and chemical inertness. Potentially, the high thermal conductivity of the material (higher than copper), may also be beneficial for some applications.

Particularly interesting applications are based on the electrical conductivity and the absence of an electronic surface barrier of the doped diamond. Such tips have been used in scanning tunneling microscopy and conducting atomic force microscopy (AFM), which has been applied for example to image nickel-filled membranes [1], or to investigate locally the electrical properties of WS₂ thin films [2]. Specialized conducting AFM techniques have benefited from diamond cantilevers as well, such as nano-scanning resistance profilometry and imaging (nano-SRP) [3,4], and breakdown voltage imaging [5]. It is anticipated that these tips will also be useful for mechanical and electronic modification of surfaces.

The microstructured diamond tips and their characterization reported in this article demonstrate the considerable flexibility with which a variety of structures can be micro-fabricated from chemical vapor deposited (CVD) diamond. Earlier [6], CVD diamond coated AFM tips and pyramidal molded tips that were part of a membrane were described, all relying on a uniform diamond coating. Here, silicon tips with a controlled selective CVD diamond coating are introduced. Also, devices with all-diamond cantilevers and tips are presented.

The CVD diamond deposition process is described in [7]. In short, it was performed by the hot-filament deposition method on four-inch wafers at a substrate temperature of 830 °C. This results in polycrystalline, high-quality films of the sp³ diamond phase with very low (down to 100 ppm) graphitic sp² content, as has been determined from Raman spectroscopy. Throughout this work, the films were in-situ boron doped, resulting in a specific resistivity in the range of 0.03 to 0.1 Ω cm, depending on boron concentration in the plasma.

These tips have withstood severe conditions, for example in the nano-SRP experiments [3,4], where typically forces of 125 μN are applied in order to penetrate the native oxide of a silicon sample, and in breakdown voltage imaging [5], where relatively high voltages are applied, causing other tip materials to wear far more quickly than diamond.

1 Diamond coated silicon tips

Silicon tips with a continuous CVD diamond coating of 100 nm thickness have been demonstrated earlier [6]. This is the minimum required thickness to ensure good homogeneity, with no pinholes observed by scanning electron microscopy (SEM).

Figure 1 shows a coated commercial [8] AFM tip. The SEM image demonstrates that coverage is continuous even for this very thin diamond film, and it displays the typical granular structure with the relatively rough surface of

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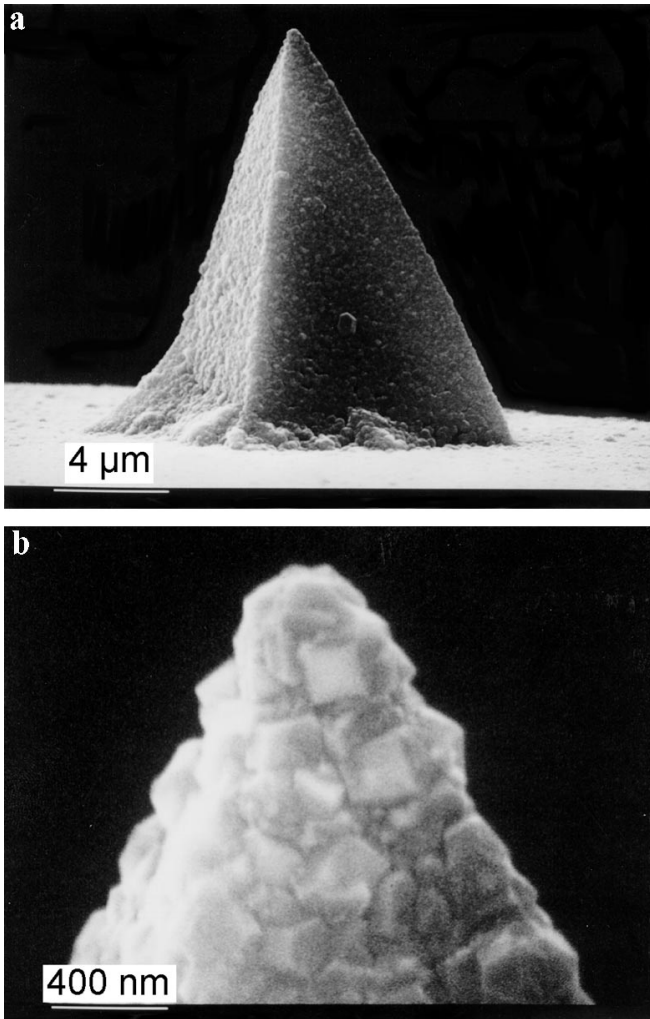


Fig. 1a,b. Diamond coated silicon tip a overall view, b close-up on apex region

the polycrystalline film. The root mean square roughness of the film is on the order of 30 nm, as estimated by AFM on $2 \times 2 \mu\text{m}$ areas on the chip supporting the lever. Consequently, the spatial resolution of AFM images taken with these tips is limited on rough surfaces, but on a flat surface, high resolution images may still be obtained due to the nanoscale roughness of the tip, with the crystallites tending to have sharp edges.

Figure 2 shows a silicon tip that has a microstructured diamond coating, covering its upper part only. Diamond can easily be distinguished from silicon owing to its higher secondary electron yield which makes it appear brighter in the SEM image. Also seen are isolated diamond grains on the silicon which are due to spontaneous nucleation. This type of selectively deposited structure will be useful when diamond tips are to be combined with other elements in a silicon based microstructure, such as actuators or sensors. The silicon tips were fabricated by anisotropically underetching oxide masked areas using KOH [9]. Local deposition was achieved by oxidizing the structures, depositing a thick photoresist from which the tip protruded, etching the exposed oxide layer, and performing a selective CVD diamond deposition [10].

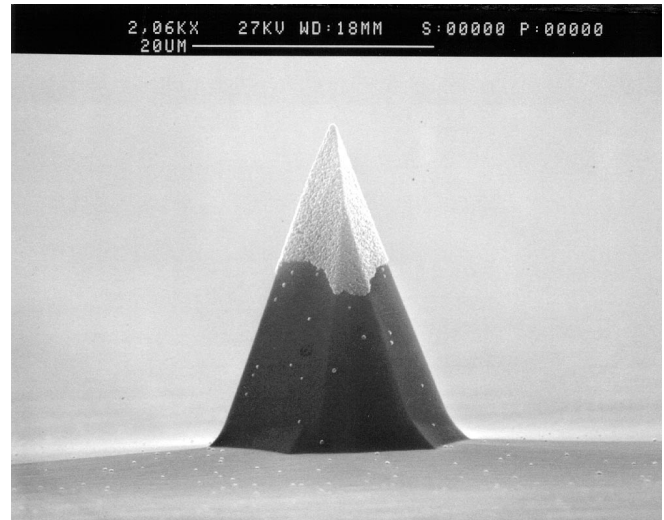


Fig. 2. Silicon tip with selective CVD diamond coating

2 Micromachined pyramidal diamond tips on cantilevers

Diamond tips of pyramidal shape on membranes, fabricated by deposition on a micromachined mold, have been reported earlier [6]. These tips have been obtained with 10 to 40 nm apex radius, and they have now been integrated with cantilevers for application in AFM.

The process flow for fabrication is shown in Fig. 3. 100 mm silicon wafers were oxidized, and square openings were photolithographically patterned. Pyramidal molds were formed by anisotropically etching in KOH and the oxide was removed. A nucleating process for the diamond growth was used with a particularly high nucleation density [7], while leaving the silicon mold completely intact. $1 \mu\text{m}$ CVD diamond was deposited and coated with a thin CVD silicon

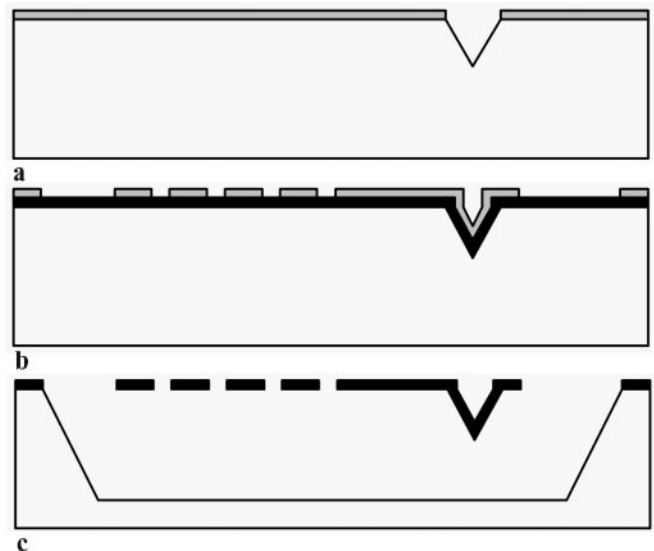


Fig. 3a-c. Fabrication process of diamond tips on cantilevers. a Oxidation of silicon wafer, patterning of oxide, anisotropic etching of pyramidal molds. b Deposition of CVD diamond, deposition and patterning of CVD oxide. c RIE etching of diamond, removal of oxide, anisotropic etching of silicon

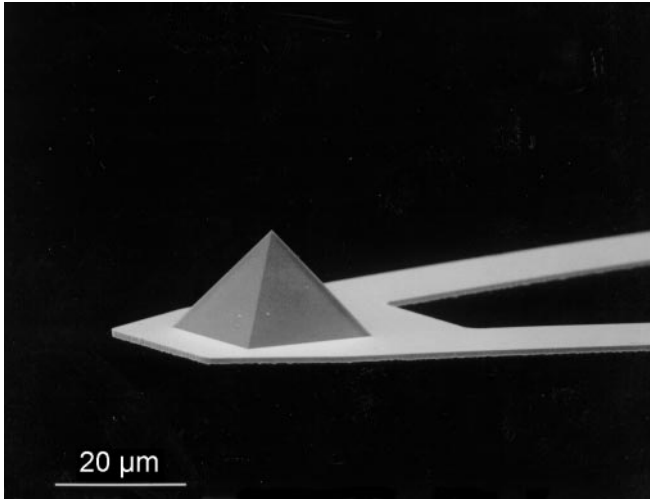


Fig. 4. Micromachined CVD diamond pyramidal probe (15 μm height) with integral cantilever

oxide film, which was photolithographically patterned to define the cantilevers and supporting membranes. The diamond film was structured by reactive ion etching (RIE) in an oxygen plasma [11]. Finally, the silicon was removed by etching in KOH. The resulting underetched membranes with the cantilevers were glued on suitable supports for testing in AFM.



Fig. 5. SEM image of the apex of a pyramidal diamond tip

A cantilever with a tip is shown in Fig. 4. Compared to the selective area deposition of CVD diamond [12], the RIE etching of the diamond results in a very precise patterning of the cantilevers.

Figure 5 shows a close-up SEM image of the apex of a tip which was made with this molding technique and which is estimated to have an apex radius of 10 nm. TEM imaging provided complementary information at higher resolution, and an example is given in Fig. 6. TEM at low magnification revealed crystallites of hundreds of nanometers. At high magnification, crystallites of a few to about 10 nm were observed near the surface, probably together with an amorphous phase. At the surface, an amorphous film was found which may contain two different layers. The outer one originates from mobile hydrocarbon species adsorbed on the sample surface that were decomposed and immobilized when they crossed the electron beam. The inner one may belong to the sample itself or may also be a contamination layer. Depending on which is true, the radius of this particular tip was estimated to be either 14 nm or 8 nm, not taking into account the contamination layer introduced by the TEM observation.

The cantilevers were designed with V shapes, with lengths ranging from 100 to 500 μm , and had spring constants from 0.1 to 10 N/m. The softest cantilevers had a resonance frequency of 11 ± 3 kHz, as predicted using the literature value of Young's modulus for polycrystalline diamond, 1050 GPa. Test structures showed the free-standing diamond film to be under a compressive strain of 1×10^{-4} .

A preliminary test demonstrating good electrical contact properties of these devices has been done. A conducting AFM experiment is shown in Fig. 7, taken on a step on a silicon substrate with a selectively grown doped CVD diamond layer, as was used to fabricate the devices themselves. This experiment was performed in air at relatively low forces ($\sim 10^{-7}$ N), and the bright areas had a contact resistance of less than about 1 M Ω . Lower contact resistances could pre-

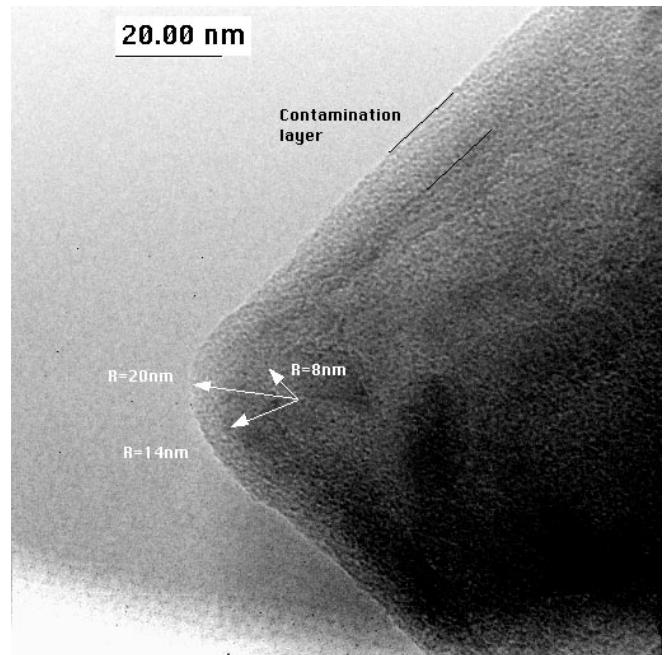


Fig. 6. TEM image at high magnification of a pyramidal diamond tip

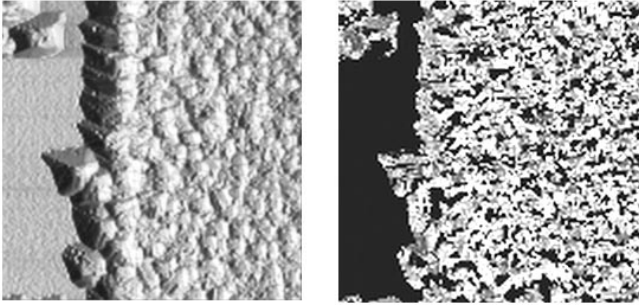


Fig. 7. Conducting AFM image taken on a selectively grown 1 μm diamond film on a silicon surface. Image area is $10 \times 10 \mu\text{m}$. Left: topography, right: conductivity (a.u.)

sumably be obtained by increasing the contact force [3]. On the silicon substrate, no current was observed.

Although qualitative first results on wear of these tips have been very encouraging, a quantitative comparison with silicon and silicon nitride tips still needs to be done.

In conclusion, two main types of structured diamond probes have been presented: CVD diamond coated tips with selective deposition on the top of the tip, and pyramidal diamond tips on levers. The pyramidal tips have been characterized in more detail using TEM. Excellent wear properties were demonstrated for all these types of tips.

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