Cleaning of diamond nanoindentation probes with oxygen plasma and carbon dioxide snow

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(Received 15 August 2009; accepted 2 November 2009; published online 7 December 2009)

Diamond nanoindentation probes may perform thousands of indentations over years of service life. There is a broad agreement that the probes need frequent cleaning, but techniques for doing so are mostly anecdotes shared between experimentalists. In preparation for the measurement of the shape of a nanoindentation probe by a scanning probe microscope, cleaning by carbon dioxide snow jets and oxygen plasma was investigated. Repeated indentation on a thumbprint-contaminated surface formed a compound that was very resistant to removal by solvents, CO_2 snow, and plasma. CO_2 snow cleaning is found to be a generally effective cleaning procedure. [doi:10.1063/1.3266972]

Nanoindentation is a widely used technique to measure the elastic, plastic, viscous, and fracture properties of materials in small volumes. A recent review covers some of the applications, usage, and current understanding of the nanoindentation technique.[1] Nanoindentation probes are typically machined as three-sided pyramids from diamond crystals, ⟨100⟩ coincident with the axis of indentation. Spurred in part by the utility and popularity of nanoindentation, the art of shaping diamonds to a three-sided pyramid has advanced to the point where most manufacturers claim an apical radius of curvature of less than 50 nm. While particular probe manufacturing processes are trade secrets, they are presumably evolved from the centuries-old art of shaping diamond crystals into tools and jewelry, as described in the recent review by Hird and Field.[2] Recent diamond-shaping progress in the open literature has largely focused on fabrication of tools for nanometric cutting and lathing; for example, edge radii of less than 10 nm have been demonstrated for lapped tool edges.[3]

Nanoindentation diamonds are in often in service for years, long after the initially sharp apex has been blunted due to the per-probe expense of diamond. The long service lives of nanoindentation probes would not be practically possible without the calibration technique first popularized by Oliver and Pharr,[1] a method which has many proposed refinements but few (if any) that challenge the philosophical roots in classical linear elasticity. The central idea is that the projected (cross-sectional) contact area of the diamond can be estimated as function of the axial distance from the apex by indentation on a material of known elastic properties; by indentation to various depths, the "shape function" of the diamond may be reconstructed. Comparison of the inferentially measured shape of the probe with that measured by scanning-probe microscopy (SPM) is an active area of research.[4–6] SPM measurements demand the highest possible cleanliness for accurate shape measurement. Cleanliness of the diamond (and indented surface) is generally desirable during routine nanoindentation testing, such that there is no interference with the diamond-target surface contact.

Some recommended cleaning techniques include washing with various solvents; indentation (or hand-pressing) of the diamond into soft materials such as single-crystal aluminum or gold, balsa wood, or cork; or dabbing with the fracture surface of a freshly broken polystyrene packing nut.[5] Pressing into adhesive tape is another method used to clean nanoindentation diamonds. These or similar procedures are shared informally among experimentalists.

SPM images of nanoindentation probe diamonds in various states of surface condition were acquired in intermittent-contact (tapping) mode. Topography images were acquired at constant cantilever mean-deflection under feedback control, with cantilever oscillation phase and amplitudes acquired simultaneously. Figures 1(a)–1(c) contrast topography, phase, and amplitude contrast images. Particles and damage are most clearly seen in the phase and amplitude contrast images, while the large variation in height obscures fine detail in the topograph. If used carefully, phase contrast can be used to distinguish the dissipative characteristics of different materials[7] and is generally more useful information. But, it was found that the quality of amplitude-contrast images in these experiments was always good, while the quality of phase-contrast images was uneven. Furthermore, phase and amplitude were found to be mostly dependent on the attack angle of the SPM probe [see the distinct three shades in Figs. 1(b) and 1(c)], giving the images the appearance of being "lit" from the right side, and the phase images were rarely more revealing than amplitude contrast. For these reasons, all images that follow are amplitude contrast.

Figure 2(a) is a SPM image of a diamond nanoindentation probe that is about 8 years old and had been used in uncounted indentation experiments. At this point, the probe has been cleaned several times in attempts to remove the contamination surrounding the apex, including overnight soaks in acetone and methylene-chloride, with frequent scrubbing by a cotton swab. Final preparation for SPM imaging was always a five-step rinse of acetone, isopropyl alcohol (IPA), distilled water, acetone, and IPA. This rinsing procedure was sufficient to prepare unused diamond probes for imaging. No significant improvement in cleanliness of the heavily used probe was found after several attempts, and, in fact, most cleanings appeared poorer than the example of Fig. 2(a).

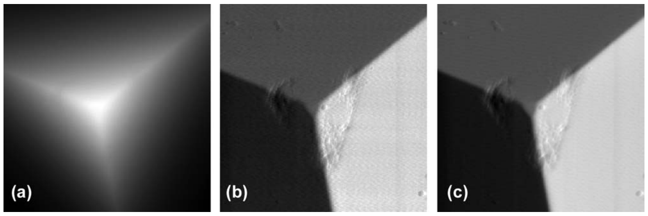

FIG. 1. (a) Topography, (b) phase, and (c) oscillation amplitude contrast images of a Berkovich diamond. Oscillation phase and amplitude are distinctly dependent on the facet being imaged. Width of field is 2.5 μm.

Based on images such as Fig. 2(a), the contamination was assumed to be of two parts: a surface layer resistant to solvent dissolution, presumably organic in origin, and small particles adhered to the surface. Removal of both types of contamination was attempted using a combination of oxygen plasma and a CO_2 snow jet. The results and cleaning mechanisms of each technique are reviewed below.

Oxygen plasma cleaning was performed with an inductive (barrel) RF plasma cleaner designed for the removal of organic contaminants on electron microscopy samples. The gas feedstock is a mixture of 25% O_2+75% Ar. Reactive-ion etching (RIE) experiments on natural diamond using a similar gas composition were shown to not affect the surface roughness.[8] Plasma conditions were 30 W with 13 mPa absolute pressure.

Oxygen ions and radicals in the plasma remove carbon by formation of CO_X, so the diamond will also be eroded during plasma cleaning. Much prior work that investigated oxygen plasma erosion of diamond utilizes RIE or other high-energy ion sources.[8–10] By way of contrast, there is no etch enhancement by high-energy ion collision in the barrel reactor used here. Other experiments performed over many hours in a barrel plasma reactor on various diamond films showed that low-energy oxygen plasmas very selectively oxidized nondiamond *sp* and sp^2 carbon over diamond (sp^3) carbon.[11] Pressure-induced conversion of sp^3 carbon to sp^2 has been observed in the wear tracks of diamond-diamond contacts[12] and is postulated to be the dominant mechanism of wear in the "soft" ⟨100⟩ direction.[2] Therefore, oxygen plasma should also be effective in removing graphitized carbon formed during normal wear. Figure 2(b) is an SPM image of the surface of the diamond after 20 min of plasma treatment, showing somewhat improved cleanliness in the near-apex region.

Figure 2(c) demonstrates the much improved cleanliness of the diamond after CO_2 snow cleaning. CO_2 snow cleaning

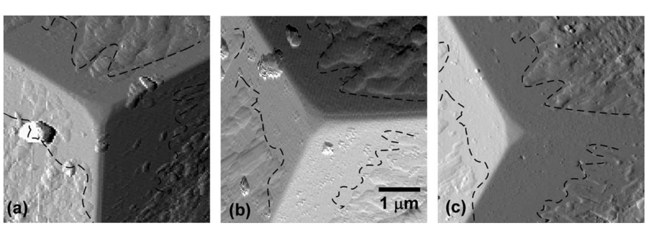

FIG. 2. Amplitude contrast images of diamond probe after (a) repeated solvent cleaning, then (b) oxygen plasma cleaning, and, finally (c), CO_2 snow cleaning. The black dotted lines were drawn to roughly outline the remaining detritus in (c), then copied to (a) and (b) to show the evolution of the diamond surface.

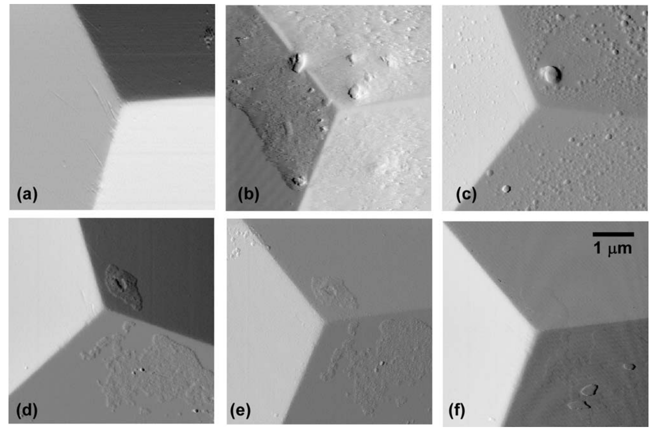

FIG. 3. Amplitude contrast images of a Berkovich diamond nanoindentation probe (a) initially clean, (b) after indentation into a fingerprint, (c) solvent cleaning, (d) snow cleaning, (e) O_2 plasma+snow cleaning, and (f) after pressing into wood+snow cleaning.

is a cleaning technique chiefly used to remove adhered particulates and organic contaminants from glasses and semiconductor wafers,[13] and has also been shown to effectively remove field-emitter sites from polished metal surfaces.[14] The snow is formed in a jet by adiabatic expansion of high-pressure gas through an orifice. The mechanisms of CO_2 snow cleaning are believed to be momentum transfer of the snow to surface particles, and solvation of organics in a transient liquid CO_2 phase that forms in the high pressures of impact.[13] A CO_2 snow jet, oriented normal to the diamond apex, should remove particles and light organics, or at least "snow plow" them to the unused part of the diamond. To prevent ice buildup on the diamond, hot air was blown over the indenter surface, and the snow jet was strafed over the diamond in a back-and-forth motion. Jet pulsing is a more sophisticated solution that prevents CO_2 ice build-up while maintaining cleaning speed and efficacy.[15]

Although the origin of the contamination on the diamond in Fig. 2 is not known, a likely contributor is sebum (the oily secretion produced by the sebaceous glands in the skin) which is composed of waxy monoesters, trigylcerides, squalene, and fatty acids.[16] CO_2 snow cleaning effectively removes fresh fingerprints,[17] yet, there is reason to believe that a more difficult-to-remove compound could be formed at the apex of a diamond probe. Each component of sebum has numerous unsaturated carbon bonds, and diamond-anvil studies have shown that crystalline organics with unsaturated bonds undergo pressure-induced saturation reactions, with the pressure needed for reaction substantially lowered by defects and disorder.[18] The mean contact pressure is the hardness of the softest material of the diamond-target pair; for calibration indentations on fused silica, this pressure is about 9 GPa, which is substantially more than the pressure needed to polymerize propylene at room temperature, 3 GPa.[18] There is also the possibility of reactivity or catalytic action by a newly exposed diamond surface from shear-derived wear.

The hypothesis that fingerprint contamination could result in a difficult-to-remove material is briefly explored here; 250 indentations into the author's thumbprint on a fused silica target were performed to a depth of 400 nm (with a different probe than shown in Fig. 2). Figure 3 chronicles the progression of the surface state of this diamond probe. The initial snow clean left the apex apparently free of contamination [Fig. 2(a)]. Note the scratches on the face that is generally oriented to the left in each image. After repeated indentation into the thumbprint-contaminated surface [Fig. 2(b)], there remains contamination that was not removed by the five-step solvent clean [Fig. 2(c)] and repeated snow cleanings [Fig. 2(d)]. O_2 plasma cleaning performed for a time sufficient to remove a felt-pen mark (nearly 30 accumulated minutes) was ineffective [Fig. 2(e)], but has apparently eroded the diamond sufficiently to remove some of the scratches. Repeatedly pressing the diamond into soft wood improves the appearance [Fig. 2(f)], but comparison with Fig. 2(e) suggests that the contaminating material was merely compressed.

A last remark: Aldrich-Smith *et al.*[6] notably recommended to *not* use ultrasonic cleaning for probes, and so this was not tried. This recommendation may possibly be because 25–40 kHz ultrasound may damage the diamond surface by cavitation shock, or could couple to a resonant frequency of the diamond and thereby cause fracture. In this regard, 100–200 kHz ultrasonic cleaners with attendant smaller cavitation bubbles may be a promising method of precision cleaning for nanoindentation diamonds. However, the expense of high-frequency cleaners is significantly greater than conventional ultrasonic cleaners, and perhaps prohibitive for infrequent use in a mechanical-testing laboratory.

In conclusion, the efficacy of CO_2 snow and oxygen plasma for the cleaning of diamond nanoindentation probes has been investigated. CO_2 snow cleaning was found to much more effective at particle and light contamination removal than solvent washing. The contamination left on a diamond after indentation on a fingerprint-contaminated target could not be fully removed with either technique, although CO_2 snow brought the diamond to its cleanest state. Oxygen plasma treatment, even when aggressive enough to erode the diamond, was ineffective at removing this fingerprint-derived contamination. The results presented here suggest that CO_2 snow cleaning of diamond probe and material under test may be good nanoindentation practice, particularly when there is the possibility of contamination by human hands.

The author thanks Professor David F. Bahr of Washington State University for the idea for this note, and a reviewer for several helpful comments and criticisms.

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