Cavitation erosion behavior of nanocrystalline diamond thin films on silicon substrates

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Diamond is an excellent material with outstanding properties like extremely high hardness, high chemical stability, wear resistance, and low friction [1]. In several specific applications, such as tools, rotary seals, electrodes, MEMS, etc., diamond is the ideal choice. However, due to its properties only very few support materials are available which have the required affinity to adhere to diamond. These are generally strong carbide forming materials like Si, Ti, Cr, W and SiC [2–7].

Recently, nanocrystalline diamond thin films have been used as electrodes in electrolyzer modules for water treatments based on electrochemical processes [8–9]. For this kind of application silicon wafers are generally used as the substrate material. In the fabrication process quality control is an important and challenging issue. A fast evaluation method is required to monitor the influence of different substrate microstructures, pretreatments and deposition parameters, on the mechanical performance of the diamond thin films.

Field tests are ideal to check the quality of diamond thin films as they provide application-relevant information. However, these tests are time consuming and expensive to perform. The well established scratch test is not appropriate to check the adhesion properties of the diamond film because the diamond tip used in this test is damaged after just a few test cycles, making it difficult to correlate and compare results [10, 11]. The Rockwell indentation technique is more suited to testing diamond thin films. However, as shown by Fan *et al.* [12], this technique is reliable only for diamond films and substrates with the same or comparable mechanical properties; this condition is not met when using a brittle substrate like silicon.

An alternative solution can be found in an ultrasonic vibratory system for cavitation charging. In literature, only a few reports exist on the use of this test for measuring the mechanical properties of diamond thin films, with many studies restricted to polycrystalline diamond films on cemented carbide substrates [13–15].

In this work, nanocrystalline diamond thin films were synthesized by the hot-filament chemical vapor deposition (HF-CVD) technique on single crystal p-type Si $\langle 100 \rangle$ wafers. The reactive gas used was methane (vol. 1%) in hydrogen. The growth rate of the diamond films was about 0.2 μm/h and their thickness was about 1 μm. (More information on the deposition parameters and diamond film properties can be found elsewhere [8, 9, 16–18].) Silicon wafers with three types of surface finish were used as substrates for the growth of the nanocrystalline diamond thin films. Depositions were performed on (1) rough, as-cut silicon surfaces with residual mechanical stresses present, (2) lapped silicon substrates characterized by an undulating topography and a lower roughness value than the as-cut silicon substrate, and (3) chemically-mechanically planarized (CMP) silicon surface, which is smooth and is normally used for the production of electronic circuits. The main topographical characteristics of the diamond thin films are listed in Table I.

The deposited thin films were tested using cavitation erosion experiments carried out in a vibratory apparatus, conforming to ASTM Standard G32-85 [19]. The vibratory frequency and the peak-to-peak amplitude were 20 ± 2 kHz and $40 \pm 1 \mu$m, respectively. The cavitation tests were performed in deionized water with a pH value of 7. The water temperature in the beaker was controlled by chilled water maintained at $20 \pm 1\,^{\circ}$C. All eroded surfaces were examined using scanning electron microscopy (SEM) and, in order to investigate the mechanism of material removal during cavitation erosion, specimens were examined after fixed cavitation intervals. The erosion damage of materials was expressed in terms of the weight loss (WL).

The dependence of WL on cavitation time for the diamond thin films (Fig. 1) on the different substrates, showed that all films exhibited negligible surface damage up to at least the first 10 min (called incubation period). After about 30 min of testing time, diamond film on the as-cut silicon substrate showed significant increase in WL followed by a linear increase of WL upon continued testing. A damage evolution of the diamond thin films on as-cut silicon substrates was conducted (Fig. 2). Rough areas on the film surface, representing preferential sites of cavitation attack constitute weak regions of the film. Formation of micrometer-sized pits (see arrow) are visible after 30 min and their location corresponds to the presence of these rough sites (Fig. 2A). The presence of these craters after 30 min of testing also explains the increase of the WL. Due to the high roughness of the underlying silicon substrate, the diamond surface is also characterized by a

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TABLE I Roughness values of the diamond thin films on silicon substrates with different surface finishings. The data were obtained by AFM roughness analysis using a scan range of 50 μm × 50 μm. The diamond film thickness in every case is 1 μm

Si (100) substrate	Mean roughness (Ra) (nm)	Maximum height (Rmax) (nm)
As-cut	259.8 ± 5.0	2743.0 ± 10.0
Lapped	185.9 ± 5.0	1738.0 ± 10.0
CMP	57.3 ± 5.0	573.9 ± 10.0

high roughness. The first pits in the micrometer range are formed at rough surface areas of the thin films. We believe that in these areas the damage also immediately affects the silicon substrate. Once these pits are formed, they propagate rapidly across the film surface producing large pores after 90 min (Fig. 2B). Increasing the cavitation time to 120 min results in further increase in surface damage (Fig. 2C), and after 150 min most of the diamond film is removed from the silicon substrate surface (Fig. 2D).

The diamond film on the lapped silicon substrate was more resistant to cavitation (Fig. 1). Here an increase of the WL was evident only after 50 min. Also, the WL increased linearly, but a subsequent drop in WL was detected after about 90 min of cavitation time. In this case, after 30 min formations of micrometer-sized cracks occur on the surface (Fig. 3A). These cracks are formed in correspondence to the rough sites of the silicon substrate. Protruding areas of the surface of the materials, characterized by an undulating topography, are weak regions of the film. Increasing the cavitation to 90 min results in the formation of micrometer-sized craters (Fig. 3B). In these regions, the damage also immediately affects the silicon substrate (see arrow) and this produces the sharp increase in WL, observed in Fig. 1. Further increase in the cavitation time up to 120 min produces strong surface damage (Fig. 3C). As in the previous case, at the end of the test the diamond thin film is completely removed from the substrate (Fig. 3D).

The diamond film on the CMP silicon substrate was the most stable of all the substrates. In this case, a small increase of WL occurred after 50 min. However, the WL remained stable upon continued testing and an increase in WL was visible only after 120 min. On CMP silicon substrates it was not possible to observe surface damage as clearly as for the films on the as-cut and lapped silicon substrates (Fig. 4). In this case, only formations of nanometer-sized cracks are evident after 30 min (Fig. 4A). In addition, once a pit is formed it does not propagate quickly across the entire film surface, indicative of good adhesion between film and substrate. After 90 min of cavitation time, micrometer-sized craters begin to form (Fig. 4B). Further increase in the cavitation time up to 120 min produces an enlargement of these craters (Fig. 4C) and, in these regions, cavitation starts to affect the substrate (see arrow). As in the previous cases, the increase of WL values (Fig. 1) was always measured in correspondence to the initiation of substrate damage. However, in sharp contrast to diamond on the as-cut and lapped silicon substrate, where at the end of the tests most of the diamond thin film is completely removed, here the film is still present on the substrate (Fig. 4D). This behavior is attributed to the low roughness of the Si substrate due to which the diamond thin film is more uniform and has better adhesion. It was found that the first damage in the nanometer range starts from grain boundaries and/or other defects (like pinholes) present in the diamond film.

To conclude, cavitation tests are useful for providing a rapid indication concerning the mechanical stability of nanocrystalline diamond thin films. For the

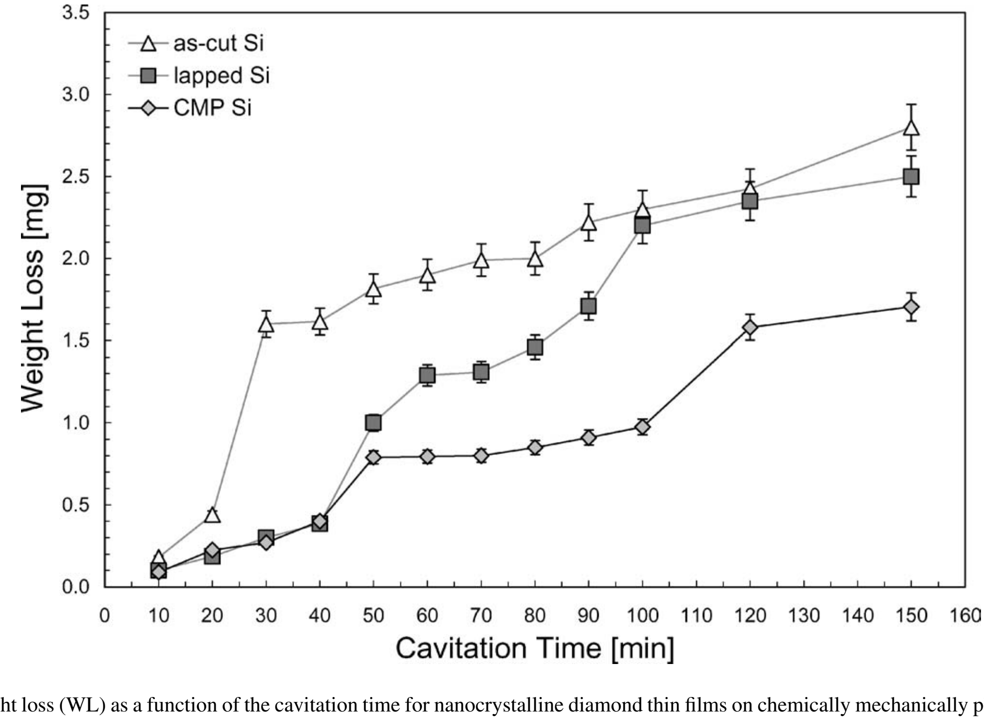

Figure 1 Weight loss (WL) as a function of the cavitation time for nanocrystalline diamond thin films on chemically mechanically planarized (CMP), lapped and as-cut silicon (100) substrates tested with a cavitation erosion apparatus.

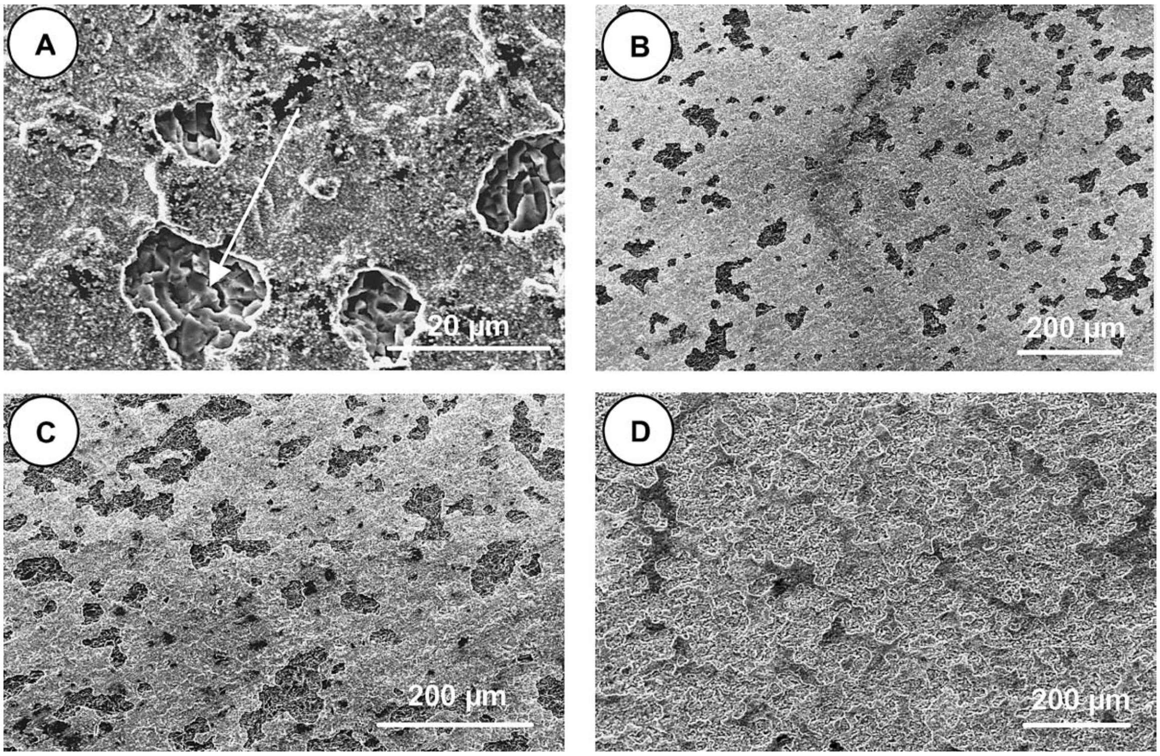

Figure 2 Scanning electron microscopy images of the eroded surface for a diamond thin film on as-cut silicon (100) substrate after different exposure times. (A) 30 min: formation of pits in the micrometer range in correspondence to the location of rough sites with an immediate damage of the substrate; (B) 90 min: propagation of pits across the film surface producing large pores; (C) 120 min: increase in the number and dimension of craters on the surface; (D)150 min: the diamond thin film is completely removed.

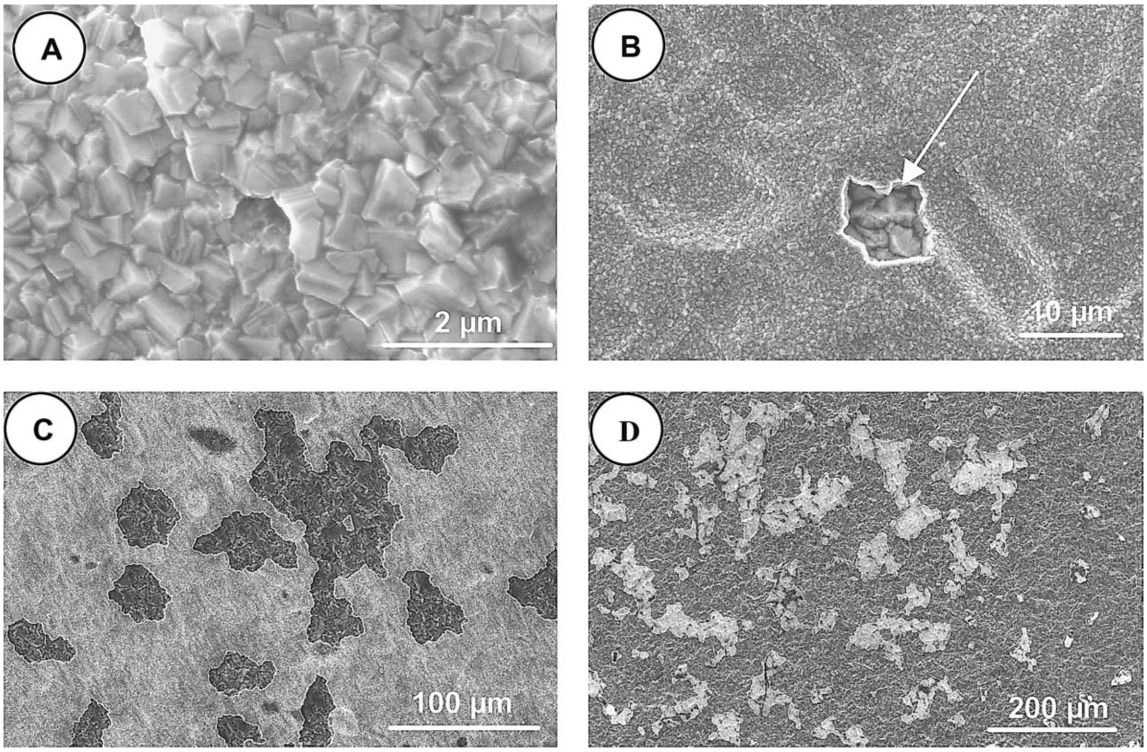

Figure 3 Scanning electron microscopy images of the eroded surface for a diamond thin film on lapped silicon (100) substrate after different exposure times. (A) 30 min: formation of cracks in the micrometer range on the surface; (B) 90 min: formation of large craters in the micrometer range and the beginNing of substrate damage; (C) 120 min: enlargement of the craters; (D) 150 min: the diamond thin film is completely removed.

tested films on differently prepared substrates, all films exhibit negligible surface damage during initial stages of testing. However, with increased testing time their cavitation behavior was significantly different. Various degrees of surface damage, in the form of material loss and increased surface roughness at weak regions in the film were observed for all samples. Results indicate that cavitation erosion resistance is inversely proportional to the roughness of the diamond thin films.

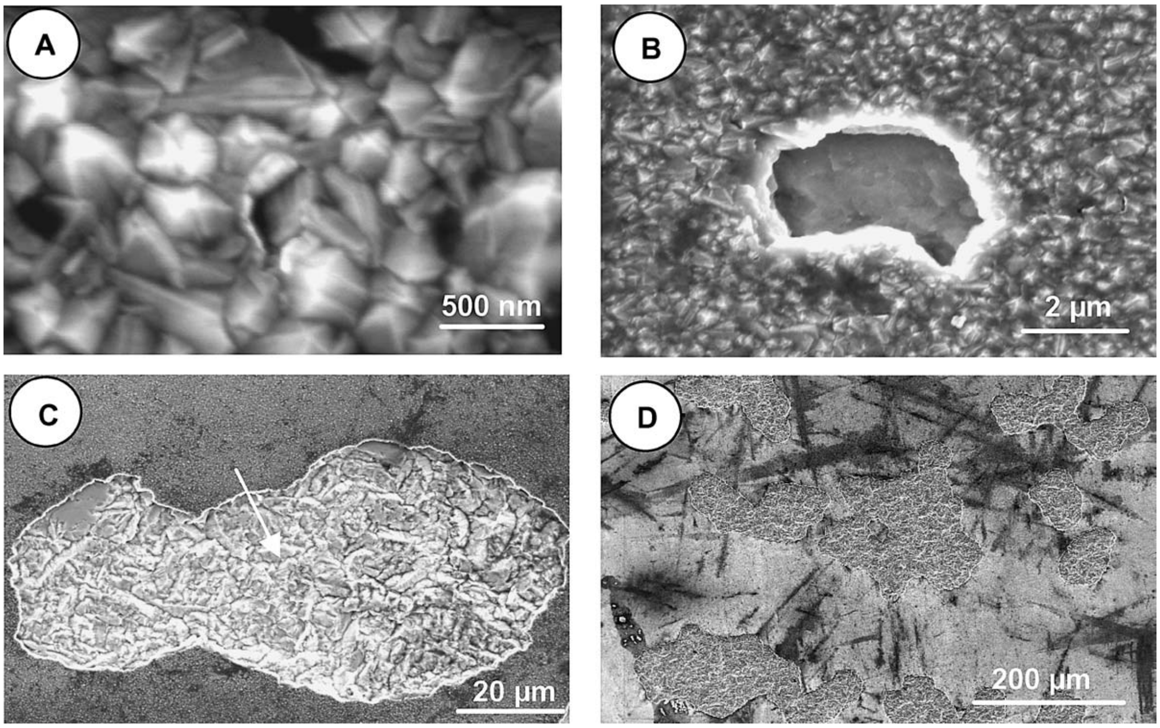

Figure 4 Scanning electron microscopy images of the eroded surface for a diamond thin film on chemically-mechanically planarized (CMP) silicon (100) substrate after different exposure times. (A) 30 min: formation of small cracks in the nanometer range on the surface; (B) 90 min: formation of craters in the micrometer range; (C) 120 min: enlargement of these craters and cavitation now also affects the substrate; (D) 150 min: there are only a few regions where the diamond thin film is completely removed.

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