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Nanostructuring of single crystal diamond by reactive and non-reactive accelerated cluster erosion

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Abstract. Reactive accelerated cluster erosion (RACE) of single crystal artificial diamond has been used to fabricate various nano- and microstructures. Carbondioxide clusters of about 1000 molecules are accelerated to 100 keV to act as the eroding agent. Using movable shadow masks, the accelerated cluster beam may erode staircase structures acting as an optical grating. A cycloid gear has been generated *via* a stationary nickel mask. Non-reactive accelerated cluster erosion using argon clusters will be considered for comparison.

PACS. 36.40.-c Atomic and molecular clusters

1 Introduction

Accelerated clusters, or nanoparticles, can be used for surface micromodification. If clusters with of the order of 1000 molecules are accelerated to about 100 keV before impinging onto a target surface, the very energetic interaction will lead to a local melting, reconstruction and ejection of material. This erosive modification can be used to structure the surface in the nano- or microscale by appropriately shielding certain areas against the accelerated cluster bombardment while others are exposed and consequently eroded. Aside from the physical erosion due to the kinetic energy transformation, suitable pairings of cluster and surface material will lead to a chemical erosion, or etching, as well. The high temperatures of several thousand kelvin achieved in the impact region for very short times will temporarily activate chemical reactions, which may lead to volatile reaction products. The technique is therefore called RACE for reactive accelerated cluster erosion [1].

The surface smoothing or polishing effect of the accelerated cluster erosion has been described already in the very first publication [2]. The effect could be explained by the investigation of isolated impacts on highly polished silicon using atomic force microscopy [3]. It turned out that an isolated impact creates on the surface a very flat hillock - instead of the expected crater [4]. The low height of these hillocks of about 1 nanometer explains at least in part the achieved smoothness. The reason for the hillock formation has been seen in the elastic rebound of the impacted material which leads to a relaxation of the transient crater [5]. Recent large-scale Molecular Dynamics calculations support strongly this explanation [6].

The microstructuring of diamond by accelerated clusters of CO_2 has been reported as a prominent example for the RACE technique since volatile CO molecules may result from the “burning” of diamond by CO_2, due to the dissociation of the molecules in the impact-induced plasma [7,8]. In this context, also the planarization of CVD diamond has been reported for the first time [7].

In the present article, further examples for the microstructuring of bulk natural as well as artificial diamond are given. The two specimen differ mainly in the fact that the available crystal faces are (111) planes in the case of natural and usually (100) planes in the case of artificial diamond. We present here staircase structures which may serve as optical gratings, also in a blazed version with inclined steps. These staircases result from successive movements of an edge shadow mask. Furthermore, a toothed cycloid wheel is machined out of artificial diamond, standing about 20 μm out of its surroundings.

Finally, we show that on the nanometer scale, the smoothness of the eroded (111) surface of natural diamond can be improved by a factor 4 by using accelerated Ar clusters instead of CO_2 clusters, avoiding thus the reactive etching process. The erosion rate, however, is then reduced by about the same factor.

2 Experiment

Figure 1 shows a schematic view of the experimental setup used for the diamond nanostructuring by accelerated cluster erosion. In comparison with earlier versions [2,3,5,7,8], the arrangement now allows to generate also clusters of lower boiling gases, such as argon, since liquid helium

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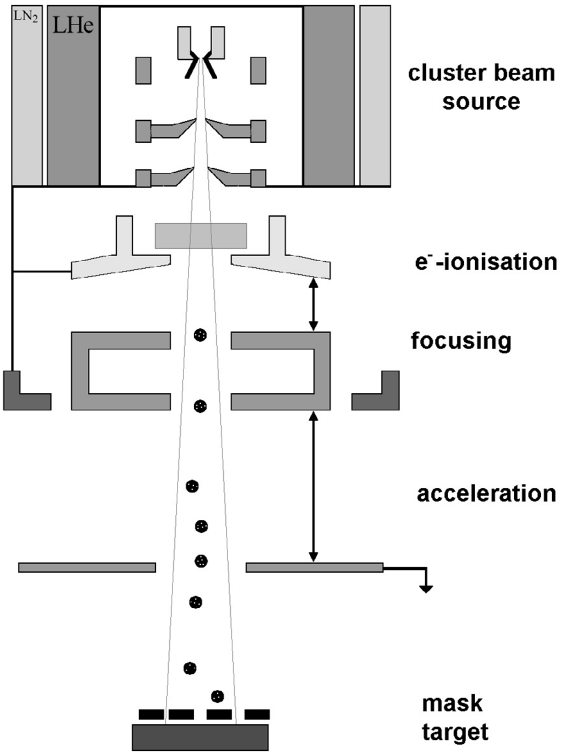


Fig. 1. Experimental setup for accelerated cluster erosion using Ar clusters.

cooling of the cryopanels for pumping the expanding nozzle gas has been installed.

The clusters are generated by adiabatic nozzle expansion of the chosen cluster gas, in the present case CO_2 or Ar, respectively. The converging-diverging nozzle has a 0.1 mm throat diameter, 10° of initial divergence, and a diverging part of 28 mm length. The core of the expanding flow forms the ionized cluster beam in high vacuum after passing two collimating orifices and traversing a sheet of 150 eV ionizing electrons. The ionized beam is focused by up to 10 kV focusing voltage before being accelerated by up to 120 kV accelerating voltage towards the grounded electrode.

The setup shown in Fig. 1 is situated in a common vacuum with no physical separation between differential pumping stages. However, the whole cluster beam generating part is on high electrical potential while the lower part of the chamber is grounded. A ceramic insulating cylinder separates electrically the two portions of the vacuum chamber. In order to avoid massive power consuming mechanical pumping equipment on high potential, the main part of the expanding gas is frozen onto cryopanels which are on high potential as well. The bath cryostats have to be filled before applying the high voltage. The amounts of the cooling liquids, nitrogen and helium, respectively, about suffice for daylong experimentation, the helium handling procedures requiring part of the time, however. The evaporating helium is transferred *via* insulating tubing to a recovering balloon and recompressed externally. The helium coolant is only necessary for low boiling cluster gases, such as Ar in the present case, which will not freeze onto a LN_2 cooled shroud.

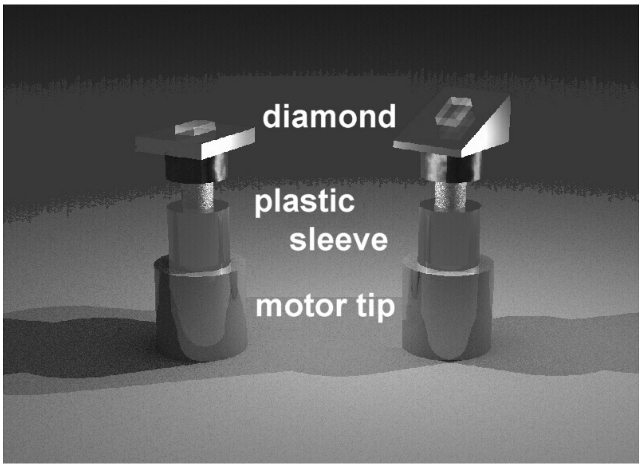


Fig. 2. Diamond fixture for staircase erosion.

The cluster mean sizes can be measured by using a dedicated time-of-flight spectrometer [9] in place of the target. In the present study, the cluster sizes are inferred from published data [10], choosing source pressures which yield approximately the same mean cluster sizes measured as number of Ar atoms or CO_2 molecules per cluster.

The structuring of the target diamond is effected *via* suitable masks which shield part of the target from the bombarding accelerated clusters. In the following, staircase structures will be shown which result from lateral displacing the edge of a shadow mask. In order to avoid a dragging of the target by the moving mask the latter should not be in contact with the target. On the other hand, it turned out that the distance between mask edge and target, the so-called proximity distance, should be as small as possible when generating staircase steps of micrometer width and submicrometer height. This can be achieved by mounting the target diamond on the non-turning top of a micromotor. Figure 2 shows the arrangements for horizontal and inclined positioning of the diamond.

Another example of the mask fixture is shown in Figure 3. Here, the mask is a nickel gear [11] that has to be mounted without any clamps or other external connections in order to project the whole toothed circumference onto the diamond. On the other hand, this mask may not move during the rather lengthy period of erosion. After several not very successful trials with gluing the mask onto the diamond a more satisfying solution turned out to be a fixture of the mask by a permanent magnet placed below the target diamond.

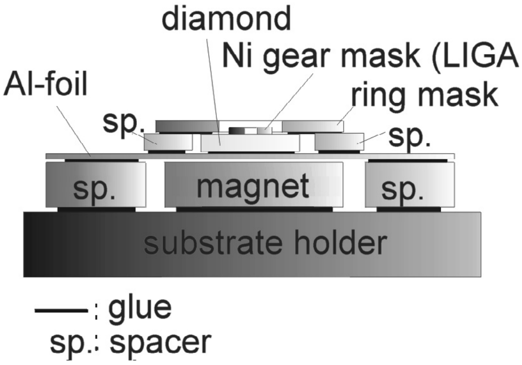


Fig. 3. Cycloid gear mask fixture.

3 Results

3.1 Staircase structures

Examples of staircase structures generated on the (100) surface of bulk artificial diamond by reactive accelerated cluster erosion with CO_2 clusters are shown in Figures 4 and 5. These images are obtained with an atomic force microscope (AFM, Digital Instruments Nanoscope III) in the contact mode. The smooth sidebands are outside the measured range. The step height of the staircase in Figure 4 is about 200 nm and the stepwidth 2000 nm. The step edges are somewhat rounded with step walls inclined against the vertical direction. The exact amount of this inclination is difficult to measure with the AFM since its tip divergence half angle is already about 30°.

Figure 5 shows the result of an inclination of the diamond against the horizontal plane by 25°. The inclination of the step walls is obviously reduced but a quantitative determination has not been tried in view of the tip divergence. In this manner, a "blazed" grating can be generated with the angle between step wall and bottom being smaller than 90°.

3.2 Surface smoothness

A comparison of natural bulk diamond surfaces before and after reactive erosion by accelerated clusters of CO_2 or non-reactive erosion by accelerated clusters of Ar, respectively, is given in Figure 6. The specimen was a flat unpolished natural diamond presenting a (111) face for erosion treatment. The pristine surface (Figure 6a) is the surface as found while Figure 6b is obtained after CO_2 and Figure 6c after Ar cluster erosion. The duration of the erosion treatment of 50 min is long enough to achieve a stationary situation. The Ar eroded surface turns out to be even smoother than the pristine natural surface while the reactive CO_2 erosion yields a somewhat rougher surface. The erosion rate, however, is down by a factor of 4 when replacing reactive by non-reactive erosion.

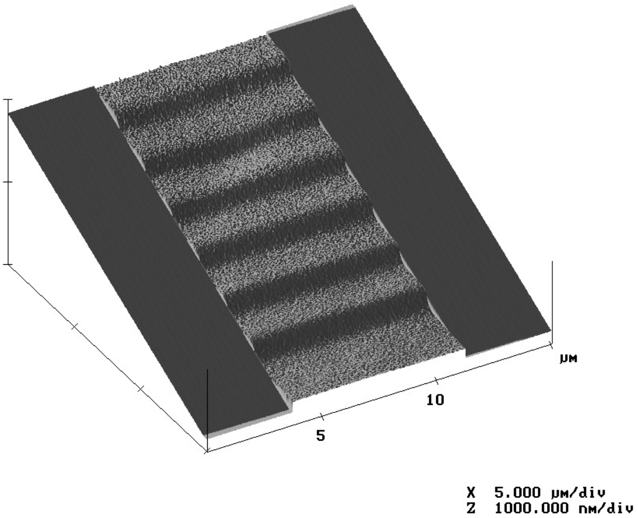


Fig. 4. CO_2-cluster eroded staircase in artificial diamond (AFM-picture).

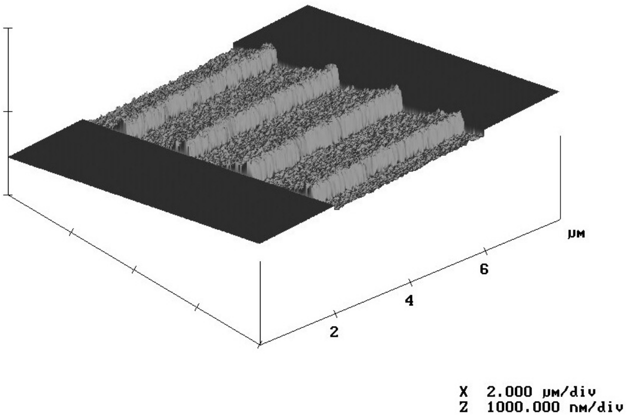


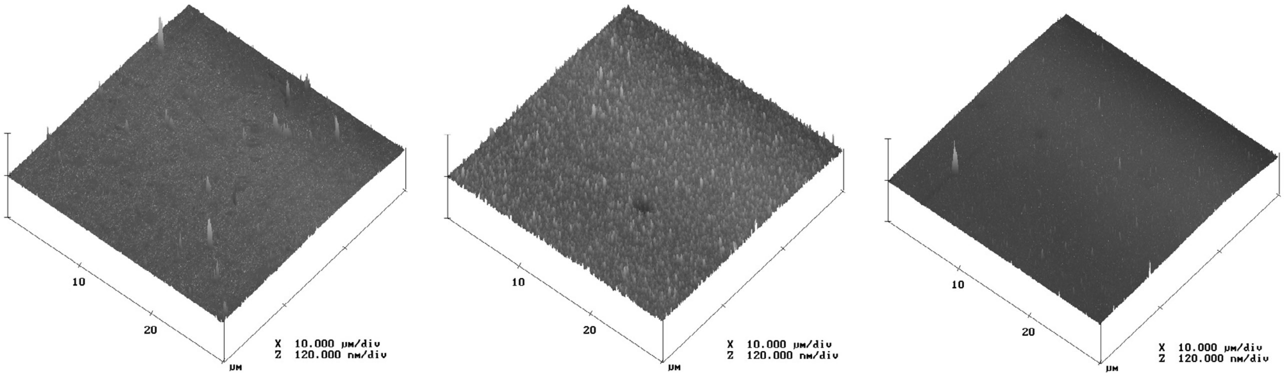
Fig. 5. "Blazed grating" in artificial diamond (inclined mounting, CO_2-cluster erosion).

3.3 Toothed wheel erosion

Figure 7 shows the result of the erosion of a cycloid gear into the (111) surface of bulk artificial diamond. The upper surface is the original surface since it was covered by the Ni cycloid mask. This toothed wheel mask has been generated *via* the LIGA process [11]. The image has been obtained by a confocal microscope (NanoFocus).

4 Conclusions

The presented examples demonstrate the potential of the micro- and nanostructuring of diamond surfaces by reactive and non-reactive accelerated cluster erosion. The surface finish as well as the erosion rate depends on the type of clusters used. Precise displacements of an edge



(a) natural pristine diamond (b) carbon dioxide cluster eroded (c) argon cluster eroded

Fig. 6. Comparison of cluster eroded surfaces with a pristine natural diamond surface (tapping-mode).

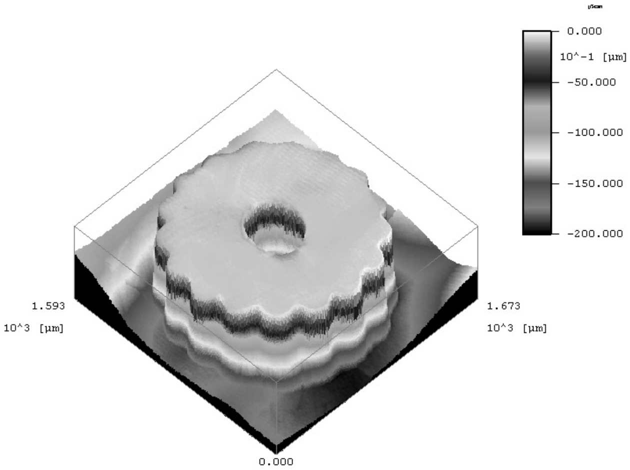


Fig. 7. Cycloid gear in artificial diamond, CO_2-cluster erosion.

mask can be used to generate gratings or staircases while a stencil mask can be used to fabricate a smoothly curved closed structure into the surface of bulk diamond.

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