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DIAMOND MICRO- AND NANOSTRUCTURING BY ACCELERATED CLUSTER EROSION*

C. Becker, J. Gspann, R. Krämer, and Y. Yamaguchi
Universität Karlsruhe und Forschungszentrum Karlsruhe, Institut für Mikrostrukturtechnik,
Postfach 3640, D–76021 Karlsruhe, Germany

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Reactive accelerated cluster erosion (RACE) has been used for direct micro- and nanostructuring of bulk diamond. Carbondioxide nanoparticles of about 1000 molecules are accelerated to 100keV energy in order to erode a staircase structure or a toothed wheel into diamond by using appropriate movable or fixed masks. Non-reactive erosion by argon clusters is slower but more effectively polishing. Large-scale molecular dynamics simulations show the nanoparticle impacts to lead to transient craters which relax to a very smooth surface via collective elastic recovery. The enhanced or reduced erosion of the respective cluster material is illuminated.

Keywords: cluster impact, nano-structuring, molecular dynamics simulation
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I. INTRODUCTION

Reactive accelerated cluster erosion (RACE) has been reported as a direct micromachining technique. Very smooth eroded surfaces result for substrates such as single crystalline silicon, glass, quartz or metals.[1] Using stencil masks, various nano- and microstructures may be generated directly, without the need for depositing and subsequently chemically developing a resist material. In our standard version, carbondioxide clusters with about 1000 molecules are accelerated to 100 keV to act as the eroding agent. Due to the high speed of about 20 km/s, the accelerated clusters as well as the constituent molecules dissociate on impact. Chemical reactions with the respective substrate material may then enhance the physical erosion. In the case of diamond, partial oxidation may lead to the volatile product carbonmonoxide.

In the present paper, examples of cluster beam eroded microstructures obtained in diamond by using stationary as well as movable masks are presented. As a distinguishing feature of this technique, the eroded diamond surfaces are always clear and transparent, meaning that the cluster beam erosion is not connected with a diamond graphitization. Furthermore, polycrystalline CVD diamond films are planarized during the erosion process.[2] This planarization extends the earlier observed smoothing of surfaces of metals[3] to higher melting insulators or semiconductors such as quartz, glass, or diamond.

Via movable shadow masks, the accelerated cluster beam has been used to erode staircase structures into bulk artificial diamond. With step heights of 200nm and stepwidths of 2000nm, such structures may act as optical gratings. The step geometries have been investigated by means of an atomic force microscope (AFM). As another example, a cycloid gear in diamond has been generated with a stationary LIGA nickel mask.

AFM investigations yielded not only the surface roughness but also the effects of single cluster impacts.[4] Instead of the expected nanocraters, hillocks with heights on the order of nanometer have been observed. Non-reactive accelerated cluster erosion using argon clusters will be compared with the reactive CO_2 cluster erosion.

Molecular dynamics simulations are launched to understand the observed nanoscale phenomena resulting from individual accelerated cluster impacts. Large-scale simulations are needed to obtain the transitory impact crater formation and their subsequent relaxation. Contrary to macro- or microscopic ballistic experiments, these nanoscopic cluster impacts are found to result in relaxed craters causing only very small surface roughness.

II. EXPERIMENTAL

Figure 1 shows a schematic view of the experimental setup used for the diamond nanostructuring by

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accelerated cluster erosion. 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 0.1mm throat diameter, 10° of initial divergence, and a diverging part of 28mm length. The core of the expanding flow forms the ionised cluster beam in high vacuum after passing two collimating orifices and traversing a beam of 150eV ionising electrons. The ionised beam is focused by up to 10kV focusing voltage before being accelerated by up to 120kV accelerating voltage towards the grounded electrode. The setup shown in Fig.1 is situated in a joint 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.

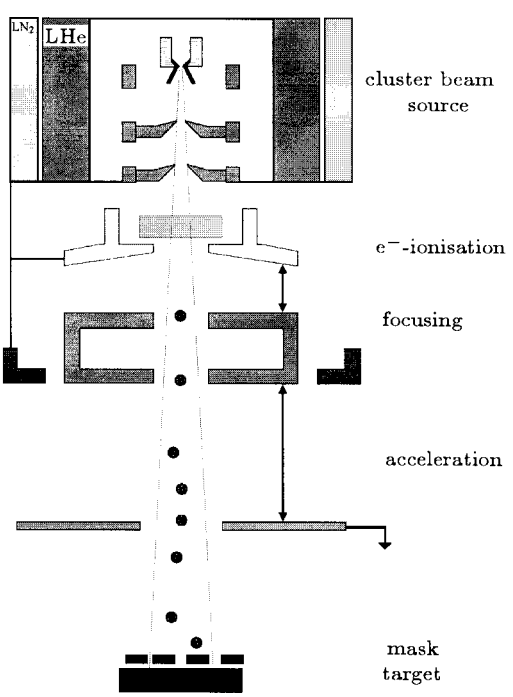


Fig.1. Schematic view of the experimental setup for nanostructuring by accelerated cluster impact.

The cluster mean sizes can be measured by using a dedicated time-of-flight spectrometer[5] in place of the target. In the present study, the cluster sizes are inferred from published data,[6] choosing source pressures which yield approximately the same mean cluster sizes measured as number of Ar atoms or CO_2 molecules per cluster.

Structuring of the diamond target is effected via suitable masks that shield part of the target from the bombarding accelerated clusters. In the following, a staircase structure will be shown which results from lateral displacing the edge of a shadow mask by means of a piezo x-y-table (Fig.2). 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, has to be as small as possible when generating staircase steps of micrometer width and submicrometer height. This can be achieved by mounting the diamond target on the non-turning top of a micromotor.[7]

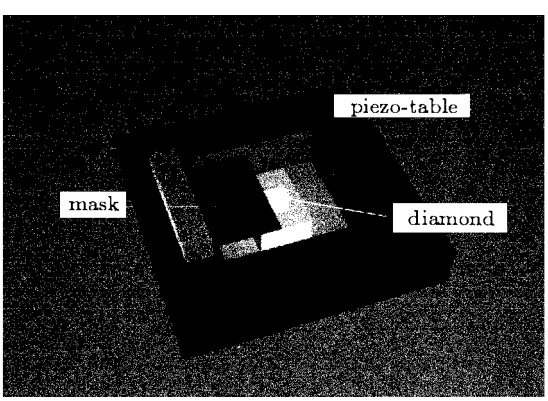


Fig.2. Movable mask fixture on a piezo x-y-table.

Another example of the mask fixture is shown in Figure 3. Here, the mask is a nickel gear[8] 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 diamond target.

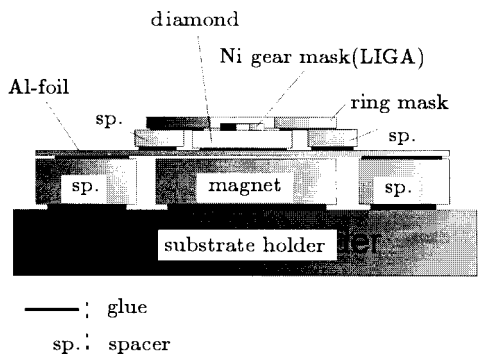


Fig.3. Fixture of a Ni gear acting as a mask for eroding a diamond gear (LIGA: microfabrication using lithography and galvanoforming[8]).

III. EXPERIMENTAL RESULTS

A. Staircase structure

A staircase structure generated on the (100) surface of bulk artificial diamond by reactive accelerated cluster erosion with CO_2 clusters is shown in Fig.4. The image is obtained by an atomic force microscope (AFM, Digital Instruments Nanoscope III) in the contact mode. The smooth sidebands are outside the the measured range.The step height of the staircase is about 200nm and the step width 2000nm. The step edges are rounded and the step walls somewhat inclined against the vertical direction. The exact amount of this inclination is difficult to measure with the AFM since the foremost part of its tip has got a divergence half angle of about 30°.

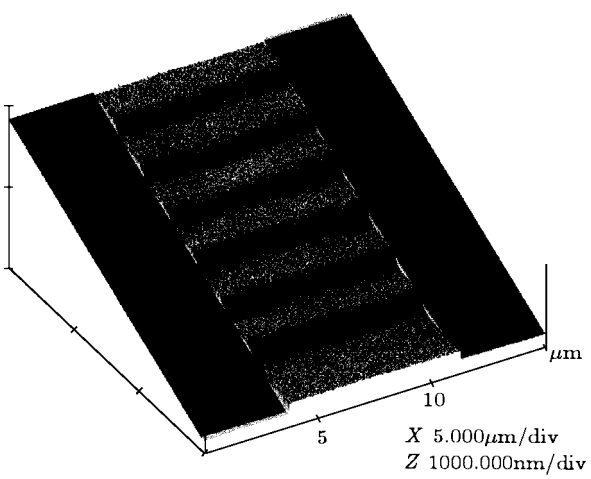


Fig.4. CO_2 cluster eroded staircase in diamond.

B. Toothed wheel erosion

Figure 5 shows the result of the erosion of a cycloid gear into the (100) surface of bulk artificial diamond. The upper surface is the original surface which was covered by the Ni cycloid mask. The toothed wheel mask has been generated by the LIGA process.[8] The image has been obtained by means of a confocal microscope (Nanofocus).

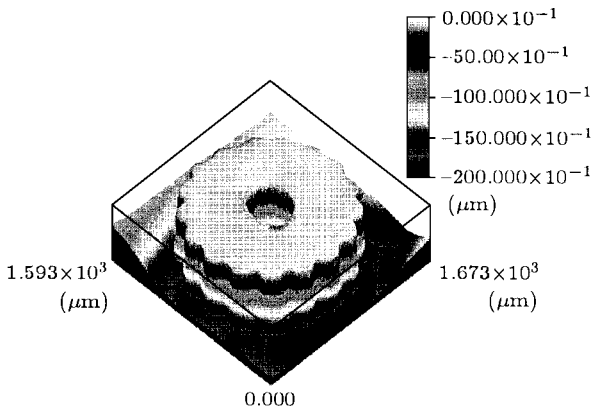


Fig.5. Cycloid gear eroded into artificial bulk diamond by CO_2 cluster impacts.

C. Surface polishing

A comparison of natural bulk (111) surfaces before and after reactive erosion by accelerated CO_2 clusters, or non-reactive erosion by argon clusters, showed that the Ar cluster eroded surface is even smoother than the pristine diamond surface while the CO_2 cluster eroded surface is somewhat rougher. The erosion rate obtained with argon clusters is a factor 4 lower than the CO_2 cluster erosion rate, however.

IV. MOLECULAR DYNAMICS SIMULATIONS OF CLUSTER IMPACTS ON DIAMOND

Large-scale molecular dynamics simulations of cluster impacts with high acceleration energy on a diamond surface were performed in order to investigate the surface erosion process. Accelerated argon or CO_2 clusters (~960 atoms, 100keV/cluster) impinge on a (111) surface of a diamond sample which consists of more than 1,000,000 carbon atoms. A hemispherical crater is fully developed about 0.7ps after the impact, and two or three-layered shockwaves are released and propagate to certain directions. However, the crater is quickly filled up with the fluidized hot carbon material due to a collective elastic recovery, even before

the reflection of the shockwaves. The impact energy of the cluster is at first transferred into kinetic energy of the impacted target material while the potential energy due to the elastic target compression is increased later. The activated carbon and oxygen atoms from the impacting CO_2 cluster seem to enhance the evaporation from the diamond surface while argon atoms seem to reflect back some of the evaporated atoms.

A. Initial and boundary conditions

The impact target must be large enough in order to avoid side effects mainly due to the impact-induced shockwave. The impact target of diamond (111) surface consists of a hexagonal fully-simulated internal region and a surrounding external region. Considering that the effect of the external region far from the impact point is not crucial to the impact phenomena, only 1/6 of the external region is simulated, and its mirror and rotated images are connected with the internal region in order to reduce the calculation time. The internal and external regions contain 758,440 and 308,240 carbon atoms, respectively (2,584,741 carbon atoms including virtual images). The vertical depth and the length of the diagonal line of the internal region are about 11.5nm and 12.2nm, respectively, and the external region extends by another 50% of the symmetric region in each direction. The outer boundary of the external region is fixed and the temperature is controlled at 300K near the outer boundary with the Langevin method.[9] The whole system was preliminary relaxed at 300K before the impact.

The impact clusters were obtained by cooling the liquid phase argon or CO_2 to 40K, and these clusters contain 961 atoms for argon and 960 molecules for CO_2, referring to our experimental data.

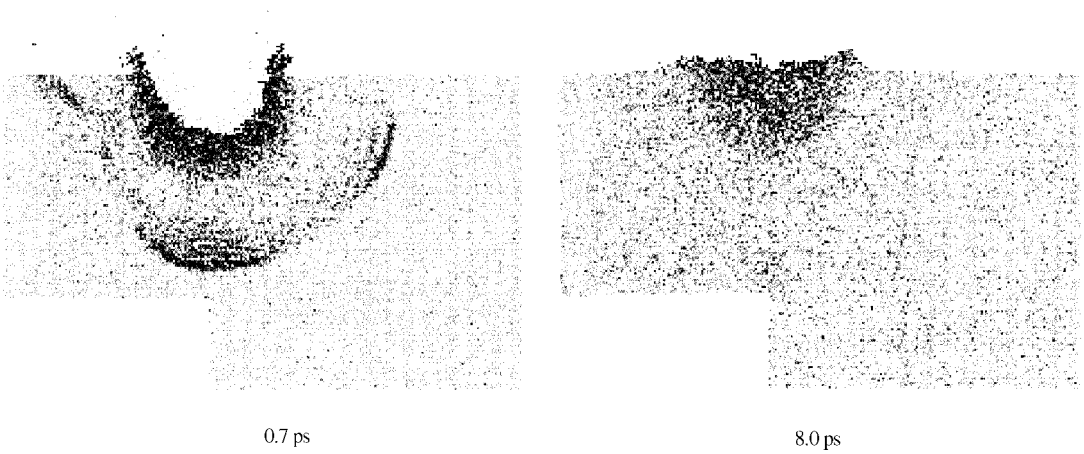


Fig.6. Snapshots of the argon cluster impact simulations (sliced view).

B. Potential functions and calculations

For the interaction between the carbon atoms the empirical potential proposed by Brenner is used.[10] While Lennard-Jones potentials are used for the C–Ar and the Ar–Ar interactions, the C–O and O–O interactions are derived from Brenner's equation assuming that an oxygen atom has initially two fixed virtual bonds automatically located at the optimum positions for real bonds. A Lennard-Jones potential is also applied for the inter-CO_2 interactions when establishing the cluster, but it is neglected during the impact simulation. Details and numerical values are given elsewhere.[11] Verlet's method[9] was adopted to integrate the equation of motion with a time step Δt of 0.2fs for the first 2ps and 0.5fs afterwards.

C. Molecular dynamics simulation results

Figure 6 shows snapshots of the argon cluster impact simulation with an acceleration energy of 100keV, where a slice of 1nm width cut perpendicularly to the impact direction is shown, and atoms with higher velocity have darker color. A hemispherical crater appears fully developed at about 0.7ps after the impact. Two or three-layered flat shockwaves propagate in the {111} directions, as elucidated further by 3D inspection. However, the crater is filled up again with the fluidized hot carbon material compressed in the hemispherical region around the point of impact due

to elastic recovery. This occurs before the reflected shockwave returns from the boundary. The shockwave goes through the impact point at about 3.0ps and the surface is mounded up, but no significant side effect can be seen because the impact point is still hot and is not recrystallized yet. The velocity of the shockwave is about 14–15km/s, a little slower than the sound velocity of 18km/s in diamond. The size of the transient crater is about 6nm in diameter which corresponds well to the size expected from macroscopic ballistic experiments.[12]

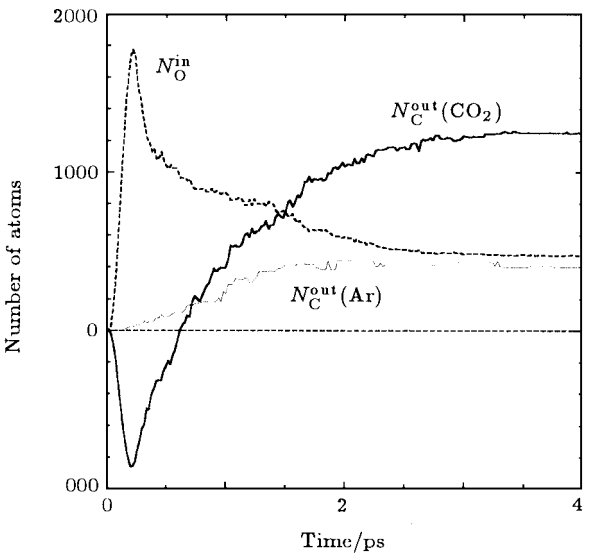


Fig.7. Simulation results: Number of evaporating carbon atoms N_C^{out} and oxygen atoms N_O^{in} at the diamond surface after CO_2 or Ar cluster impact.

The difference between the argon and the CO_2 cluster erosion appears in the motion of the surface atoms after the crater relaxation. For the argon cluster impact, the evaporation of carbon atoms from the surface is suppressed in the vertical direction by the argon atoms. On the other hand, the activated carbon and oxygen atoms stimulate the evaporation by taking carbon atoms away from the surface after the CO_2 cluster impact. The number of carbon atoms leaving the diamond surface is shown for both impacts in Fig.7, together with the number of oxygen atoms remaining near to the diamond surface after the CO_2 cluster impact. The number of carbon atoms escaping from the surface is more than three times larger for the CO_2 cluster impact than obtained for the argon cluster impact, in rather good correspondence to our earlier mentioned experimental factor 4.

V. CONCLUDING REMARKS

Direct nano- and microstructuring of diamond has been achieved by reactive accelerated cluster erosion (RACE) with CO_2 clusters, or its non-reactive version using Ar clusters. Precise displacements of a movable mask have been used to generate staircase structures for optical gratings while a fixed stencil mask served to fabricate a smooth closed structure, a cycloid gear, into the surface of bulk diamond by means of CO_2 cluster impact erosion. With argon clusters, a better surface finish but a slower erosion have been observed. Large-scale molecular dynamics simulations were undertaken in order to investigate the surface erosion process. Transitory hemispherical impact craters have been found to relax by elastic rebound of the fluidized carbon material to yield the smooth eroded surfaces. CO_2 clusters are found to stimulate the escape of carbon while argon clusters seem to reduce the evaporation from the diamond surface.

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