Diamond nucleation on cleaved Si(111)

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Diamond crystallites have been nucleated and grown by hot filament chemical vapor deposition at 600 °C on the untreated fracture surface of a cleaved Si(111) sample. The flat surface of the cleaved crystal was inactive towards diamond nucleation while, on the terraced surface formed by the propagating crack, a high density of nuclei was found. The crystallites were nucleated in correspondence of edges between (111) terrace planes and step planes. The occurrence of edges, as determined by scanning electron microscopy (SEM) observation, is a necessary but not sufficient condition for the nucleation and this fact suggests that particular atomic arrangements are required for the diamond nucleus formation.

The role of substrate pretreatment in enhancing the nucleation density in the diamond deposition from the gas phase is still unclear. In fact, the effect of surface scratching by abrasive powders is currently a matter of debate, as well as the role of carburization reactions occurring at the surface of carbide former substrates. Several authors claim the presence of seeds in explaining the enhanced nucleation on substrates as different from metals, silicon, or glass which are submitted to scratching by diamond paste or to ultrasonic activation with diamond powder suspension.[1] The previous deposition of amorphous hydrogenated carbon (*a*-C:H) has been demonstrated to be effective in enhancing the nucleation density of diamond, but to a limited extent only.[2,3]

In a recent paper, Dennig and Stevenson[4] reported that the nucleation of diamond from the gas phase in the hot filament assisted chemical vapor deposition (HFCVD) may occur on locations that protrude from the surface, such as edges or apexes. They reported that the diamond nucleation on unscratched silicon substrates is independent of the way the surface topographical patterns were produced. In the case of molibdenum substrates abraded with diamond paste prior to the deposition process, the authors found that on scratches having round-shaped edges, the diamond nucleation did not occur. These authors stated "although residual diamond abrasive powder may enhance nucleation, our results show that nucleation is promoted by topographical features alone ... the presence of some residual abrasive is not necessary to initiate nucleation."

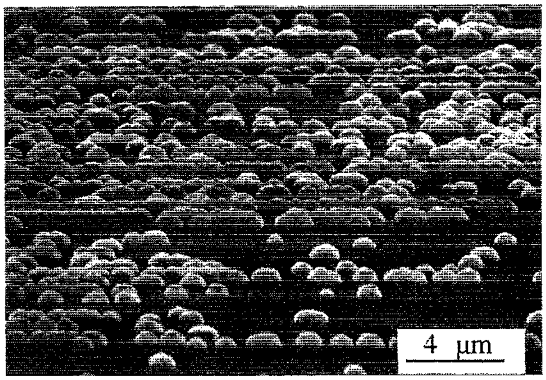
The results reported in this communication partly support those findings and confirm that seeding is not the only way to explain the increased nucleation density on substrates submitted to scratching with diamond paste.

Diamond crystallites have been deposited by tantalum HFCVD on a Si(111) crystal cleaved in air with chisel and hammer. Due to the exposure to atmosphere, the resulting Si surface is expected to be covered by a layer of native oxide, SiO_x ($x<2$), whose thickness is in the range of 12–30 Å[5] and by several monolayers of water, weakly bound, that desorb at temperatures higher than 200 °C.[6]

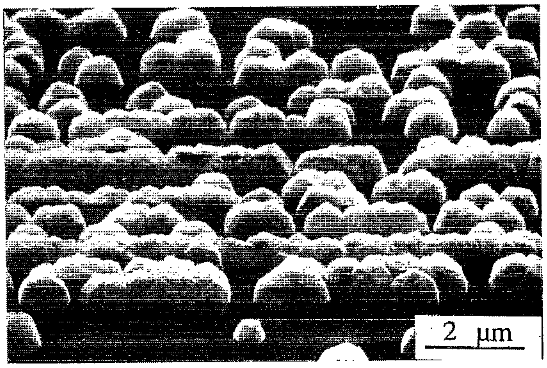
The specimen was washed by acetone in an ultrasonic vessel and then inserted in the deposition chamber,[7] without any abrading treatment.

The deposition process was carried out according to experimental conditions that ensure the formation of the diamond phase only[8] (2.0% v/v CH_4 in H_2, total flow rate 100 sccm, $P=76$ Torr, filament temperature = 2180 °C, and substrate temperature = 600 °C). Substrate to filament distance was 6 mm and the deposition time 1 h.

Following the deposition process, the sample was observed by SEM. The microscopic observation showed that the fracture surface was a flat plane except near the notch, where many cleavage steps were present. The steps visible



(a)



(b)

FIG. 1. Nucleation of diamond on the Si(111) terraced surface produced by cleavage: (a) top view of the decorated "staircase," (b) particular view of diamond crystallites (tilt = 55°).

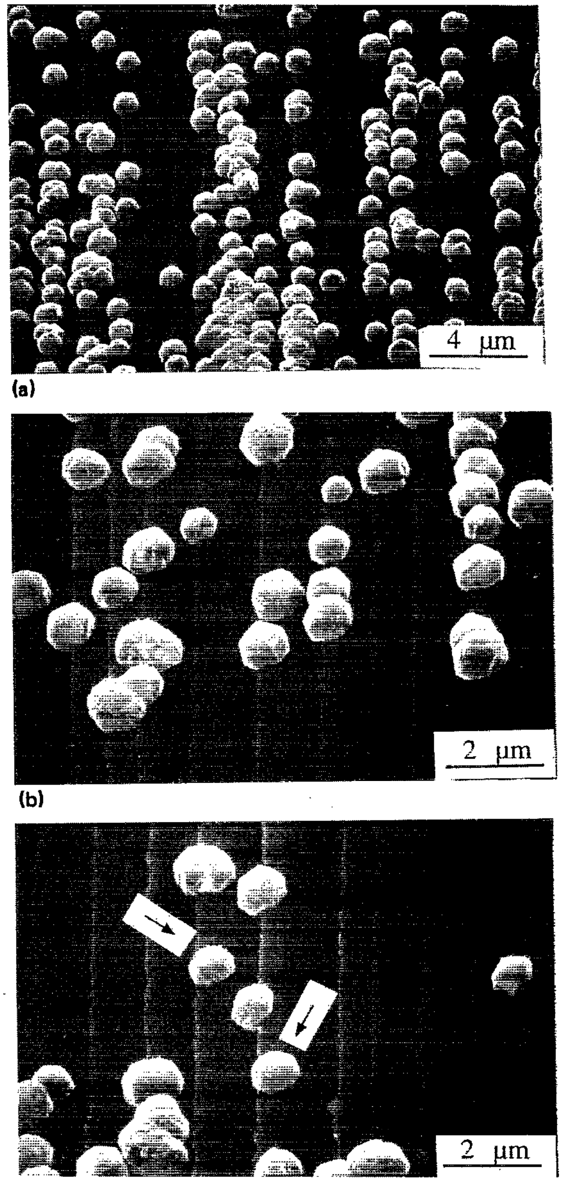


FIG. 2. Lateral view of the terraces: picture (a) represents a general view; in (b) the edge nucleation is shown; the crystals indicated by an arrow in picture (c) were nucleated on edges formed by a substep and the terrace.

on a cleaved surface may arise for several reasons. They may result from the intersection of a cleavage crack with a low-angle boundary containing a grid of closely spaced screw dislocations, all of the same sign.[9] In that case large-sized steps, observable by an optical microscope, develop in the cleavage plane giving rise, at the low-angle boundary, to characteristic river patterns. Another possibility is simply due to the fact that, in the case of specimens fractured by a hammer and a chisel, if the cleavage crack starts in such a manner that the crack is not parallel to the cleavage plane, the steps are formed in such a way to accomodate the misalignment. The latter mechanism is probably the most effective in the present case.

On the flat surface of the sample, no diamond nucleation was observed. On the contrary, on the stepped sur-

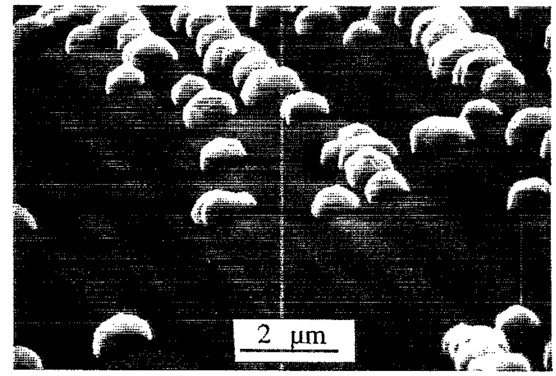


FIG. 3. SEM picture of (111) terraces (lighter planes) and steps (darker planes); the different contrast is due to the fact that the secondary electron yield is proportional to $1/\cos\beta$, where β is the angle between the primary electron beam and the normal to the surface.

face, a conspicuous diamond nucleation occurred (up to 10^7–10^8 nuclei/cm^2). Nucleation behavior is visible in Figs. 1(a) and 1(b) where the top view of the diamond-decorated "staircase" is shown. Figures 2(a) and 2(b) show that the steps are about 1 μm wide and that diamond crystallites nucleate in correspondence of edges. No nucleation has been observed on Si(111) terraces. In Fig. 2(c), the crystals marked by arrows were nucleated in correspondence of substeps present on terraces.

Several diamond crystals exhibit well-defined flat (100) faces and the analysis of their layout does not show any preferred crystallographic orientation with respect to the silicon substrate.

The edge nucleation is more evident in Fig. 3, where a different tilting of the sample allows one to confirm the above mentioned findings. In this micrograph, the lighter terraces correspond to (111) planes. The darker planes indicate that the height of the steps is of the same order of magnitude as the terrace length.

The stepped surface produced during the cleavage process presents features similar to those prepared by topography patterning techniques[4] but, as shown in Fig. 4, the presence of edges is a necessary but not sufficient condition

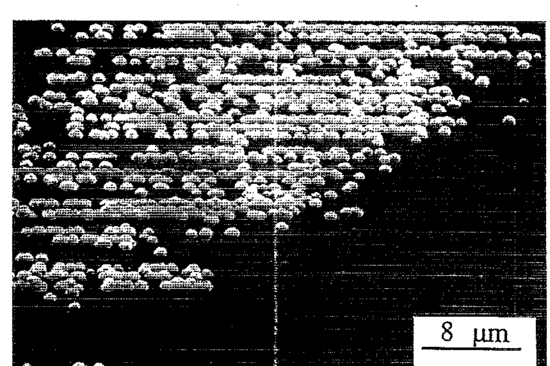


FIG. 4. Terraced region of the surface where inhomogeneous nucleation occurred.

for diamond nucleation in that on several stepped zones, no diamond nucleation has occurred. The rationalization of this fact requires further investigations in order to determine the particular atomic arrangements at the edges. In fact, the step-edge geometry depends on the crystallographic direction of the edge itself.[10,11] This [*uvw*] direction is determined by what kind of (*hkl*) plane interesects the (111) terrace plane (in fact: $u=l-k$, $v=h-l$, $w=k-h$) and by the presence or absence of kinks.

In conclusion, the present communication shows that high nucleation densities can be obtained on silicon substrates without the need of seeding by diamond powder. These results confirm the findings reported by Dennig and Stevenson[4] and, in particular, show that Si(111) terraced surfaces present edge structures suitable for diamond nucleation.

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