On the occurrence of \{113\} facets on CVD-grown diamond

G. Janssen, J.J. Schermer, W.J.P. van Enckevort \(^1\) and L.J. Giling

*Experimental Solid State Physics III, University of Nijmegen, 6525 ED Nijmegen, Netherlands*

Received 8 May 1992; manuscript received in final form 17 July 1992

Relatively thick films of diamond were deposited homoepitaxially on cylindrical substrates from an acetylene—oxygen combustion flame. On these single crystals a number of stable F faces are present. For the first time stable facets other than \{111\} and \{100\} are observed, namely \{113\} facets. These facets occur under conditions of low surface coverage, e.g. at high deposition temperatures. This confirms the prediction of a previously developed crystal growth model. A preliminary investigation of the relative stability of the \{113\} faces as function of the deposition temperature is described.

I. Introduction and theory

The power of sphere-growth experiments for the investigation of fundamental crystal growth phenomena, and especially the relative stability of the crystal faces, is well known [1—3]. Gardeniers and co-workers [4] have performed very extensive experimental and theoretical studies on the chemical vapour deposition (CVD) of silicon on hemispherical substrates. They observed only flat faces with indices \{hhk\}. The reason for this is the very high stability of the \{110\} periodic bond chains (PBCs [5]), which are the basic entities of these \{hhk\} faces. Because of this, all surfaces in the \{110\} zones have a potential S character. Gardeniers et al. argued that the absolute density of adsorbed species on the slightly misoriented surfaces [7]. Thus, above a certain critical coverage the \{113\} faces will become rough. The surface coverage will increase

\(^1\) Present address: Solid State Chemistry, University of Nijmegen, 6525 ED Nijmegen, Netherlands.
upon lowering the temperature, from which it can
be concluded that the \{113\} faces will not grow
planar below a certain critical temperature. This
temperature is called the "chemical roughening"
temperature, to distinguish it from the well-known
"thermal roughening" temperature (see, e.g., ref.
[8]). Similarly, the surface coverage and thus the
appearance of the \{113\} faces can be changed by
varying the composition of the gas phase, in the
case of silicon deposition, by changing the Cl/H
ratio [9].

The observed, relative stability of the \{113\}
faces as a function of the temperature and the
Cl/H ratio [1,9] is in remarkably good agreement
with these theoretical predictions. For total sur-
face coverages ($\theta_{\text{total}}$) below approximately 0.8
these facets are flat F faces. That is, the (polar)
plot of the surface tension versus the crystallo-
graphic orientation shows a cusped minimum in
all directions for the \{113\} faces. For $\theta_{\text{total}} \geq 0.8$
only macrosteps parallel to the \{110\} PBCs are
observed, while the surface is curved in the per-
pendicular direction. This implies that the sur-
face tension has a cusped minimum only in the
direction parallel to the PBC. Or in other words:
at low surface coverage all steps on a \{113\} face
have positive step free energies and thus will not
form, while for high surface coverages the step
free energy becomes negative for all steps except
those parallel to the \{110\} PBC. In this last case
an S face has been formed. Although not explic-
tly stated in the theoretical studies of Gardeniers
on silicon [4], it can be derived from this work
that under most growth conditions all faces in the
\{110\} zones are S faces with steps parallel to the
in-plane PBC. Therefore, these regions will ap-
pear as curved, stepped S zones in virtually all
sphere growth experiments. This is quite under-
standable, because in order to form steps perpen-
dicularly to the PBC and thus give the face a K
character, the stable PBCs should be broken up
which requires large amounts of energy.

A few more remarks are in place here. Firstly,
the theory on the stability of different faces was
derived under the assumption of near-equili-
rium crystal growth, that is for low supersatu-
rations. Secondly, it should be noted that after a
sufficiently large crystal has developed only facets

corresponding to the absolute minima in the sur-
face tension will remain. All other faces, which
we have called flat and stable here, are in fact
only present in a transition phase from the origi-
nal seed to the final crystal. Thirdly, unfortu-
nately the theory does not predict the occurrence
of \{110\} facets and the wealth of facets with
higher Miller indices (e.g. \{337\}, \{331\} and \{551\})
that can be observed experimentally on hemi-
spheres overgrown by silicon CVD [1].

As diamond and silicon have the same crystal
structure and the (1×2) reconstruction is known
to occur for diamond as well [6,10,11], the above
summarized theory could also apply to diamond.
Without going through the surface tension calcu-
lations again it is clear that the same general
rules should govern the growth of diamond at
least in a qualitative manner. Indeed planar \{111\}
and \{100\} faces are generally observed on poly-
crystalline diamond films. To the best of our
knowledge no other F faces were ever reported
for CVD grown diamond. This is not very surpris-
ing as it is rather difficult to determine the crys-
tallographic orientation of the individual faces in
a polycrystalline layer. The crystals in such layers
are often truncated and the shape of the facets
can be influenced by interactions with the neigh-
bouring crystals and by twinning. Moreover, these
tiny crystals have already reached their final
shape, with only those faces present that corre-
spond to the absolute minima in the growth rate.

Based on the theoretical calculations described
above the \{113\} facets are expected to develop
under growth conditions where the crystal sur-
faces are relatively clean. However, during nor-
al diamond deposition the conditions are such
that the surface will be almost completely cov-
ered by hydrogen and the growth precursors [12–
14]. This is caused by the extreme non-equili-
rium condition of the gas phase necessary for
good-quality diamond deposition. The gas phase
concentrations of both atomic hydrogen and many
hydrocarbon radicals are often orders of magni-
tude higher than the heterogeneous equilibrium
concentrations at the deposition temperature. All
of these radicals have high sticking probabilities
on the diamond surface. The desorption rate of
the radicals is low because of the relative low
deposition temperatures (800–1000°C). These reasons lead to a surface coverage very close to unity, which would inhibit the occurrence of \{113\} faces. Indeed we have reported on a sphere-growth experiment in a hot filament assisted CVD system, for which no \{113\} facets were observed [3]. The surface coverage during this experiment at a deposition temperature of 920°C was certainly above 0.8 [14].

Recently it was shown that good quality, homoepitaxial deposition of diamond can also be performed at much higher temperatures (1200–1500°C) in high power, high growth rate environments such as an acetylene–oxygen flame [15] or a plasma torch [16]. With this we arrive at the objective of the present work: can \{113\} faces be formed in diamond sphere-growth experiments under conditions of low surface coverage?

2. Experimental setup

An acetylene–oxygen flame deposition setup was employed, which has been under development in our group for the last two years [17]. In this system, the deposition temperature can be controlled (within ±10°C relative) and measured (within ±20°C absolute) with considerable accuracy during long term experiments. Because of the large temperature and concentration gradi-

Fig. 1. Micrographs of a single crystal diamond grown in 1 h at 1190°C and \(S_c = 2.9\%\). (a) SEM micrograph viewing along [\bar{1}10] direction. (b) SEM micrograph at an angle of \(= 30°\) with the [110] direction, that is roughly in top view of the (311) facet. (c) SEM micrograph of the (311) facet, in top view. (d) Nomarski differential interference contrast micrograph of the same (311) facet as in (c).
ents existing in the flame, a variant of the sphere growth experiment was used, namely a "cylinder growth" experiment [18]. A thin cylinder (0.25 mm thick) was laser-cut from a slice of natural type IIa diamond. The base of the cylinder was chosen to have an (110) orientation (less than 2° off). Therefore, the wall of the cylinder exhibits all possible orientations in the [110] zone, while on the rim of the cylinder all orientations between this zone and the (110) plane are available. The wall of the cylinder is not smoothly curved but somewhat corrugated. This is caused by the laser cutting process which produces grooves, approximately 20 μm wide and 4 μm deep, perpendicular to the base plane. Because of the high growth rates (typically 150 μm/h for the (110) faces) and the relative thick layers deposited (typically ≥ 60 μm for all orientations), the roughness of the cylinder wall does not hamper the experiments. The base of the cylinder had a surface roughness of less than 20 nm. The cylinder was soldered to a molybdenum substrate holder ensuring a good thermal contact. The diamond was placed in the central axis of the flame. For polycrystalline diamond films deposited under similar conditions in one hour or more, it was found that the central area (diameter 3 mm) of these films is homogeneous within 10%, both in quantity and in quality [17]. By using small cylinders, which had a diameter of only 1 mm, uniform growth conditions over the complete cylinder could be ensured. Indeed, in none of the experiments were peculiarities caused by any inhomogeneity in the growth observed for the crystal surfaces directly facing the flame.

3. Results and discussion

On a number of these cylinders, a homoepitaxial film with a thickness between 60 and 150 μm was deposited. The range of the deposition conditions is given in table 1. The deposits were investigated by SEM and optical – Nomarski differential interference contrast – microscopy. Figs. 1a and 1b show, in top-view and at an angle of ≈ 30°, respectively, SEM micrographs of a diamond crystal grown in 1 h at 1190°C, using a carbon supersaturation $S_c$ [19] of 2.9% (sample 1). The thickness of the layer in the [110] direction is $150 ± 10 \mu m$. In the top-view, the crystal has a truncated octagonal shape, as was also observed by Snail and Hanssen [15]. The (110) base face is still present and has a cobbled structure, as is typical for this K/S face (refs. [16,19,20] and references therein). Actually, for all samples investigated here, the (110) face consists of small, homogeneously distributed pits, typically 5 to 10 μm across, with planar side walls. Most probably these side walls have {100} and/or {111} orientations, but a more elaborate study is necessary to determine the exact orientations.

Along the rim of the cylinder a number of flat facets have developed (fig. 1). The boundaries of all these facets are sharp. An exception are all the boundaries with the original (110) face, which reflect the pitted structure of the (110) face. Also the boundaries of faces with the bottom part of the seed crystal are not well defined, probably because of problems in the transport of growth species towards the lower parts of the seed crystal. The crystallographic orientations of the facets can be determined by X-ray analysis or optical goniometry angle measurements, but these methods are rather cumbersome. The orientations can be determined much faster from the crystal and surface morphology in relation to the crystallographic symmetry, as will be shown below. The orientations of the main facets of the sample in fig. 1 were also verified by X-ray analysis. For

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<td>Details of experimental setup and the range of deposition conditions used</td>
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<td>Welding torch</td>
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<td>$O_2$ flow</td>
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<td>Carbon supersaturation ($S_c$)</td>
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All four \{113\} facets make an angle of 31.5° with the \(110\) plane, and angles of 25.2° and 29.5° with the neighbouring \(100\) and \{111\} faces, respectively. Fig. 1c is a close-up of fig. 1b showing the \{311\} facet in more detail. The rims of this facet are parallel to \{011\} and \{112\} directions. The angle between the rims determined for all four facets was 75° ± 3°, in good agreement with the theoretical value of 73.2°. Inspection by differential contrast microscopy of the same facet (fig. 1d) shows that the facet is covered by macrosteps. Such macrosteps, parallel to the in-plane \langle 110 \rangle PBC, were observed on all \{113\} facets. Most of the higher macrosteps run across the full width of the facet, but some lower steps seem to be confined to the central region of the facet. From focusing the optical reflection microscope it was determined that the facets are slightly curved perpendicular to the PBC direction. The angle enclosed by the (180 µm wide) facet is 2.5°, which is considerably smaller than the 20.7° for the original seed crystal. Still, the presence of this curvature shows that the stabilizing effect perpendicularly to the \{011\} PBC is relatively weak.

No \{110\} facets, apart from the starting \{110\} face, nor any other flat face – not mentioned above – were observed on this specimen and most other specimens. The growth rate in the \langle 110 \rangle directions \(R_{110}\) for this crystal was 150 ± 10 µm/h. From the sizes of the different F faces, the relative growth rate of a \{hkl\} face \(X_{hk1} = R_{hk1} / R_{110}\) can be determined. In this case \(X_{111} = 0.39 ± 0.08\), \(X_{100} = 0.46 ± 0.08\) and \(X_{113} = 0.6 ± 0.1\).

The results described above were reproduced for a number of samples. The deposition conditions were varied slightly in these experiments. Although the size of the facets and thus their relative stability changed slightly between different samples, we were not able to find a clear relation with any of the growth parameters from this preliminary investigation. This probably means that most parameters are in someway coupled to each other. In addition, it was not possible to draw conclusions from experiments in which the growth conditions were changed more dramatically. Such experiments resulted either in rather thin deposits with undeveloped facets, or
in a completely deteriorated growth with badly shaped or non-distinguishable facets. The only exception were the experiments in which the deposition temperature was varied.

As the transformation of the \{113\} face is governed by the surface coverage, the stability of this face should change with the deposition temperature. For this reason, a series of experiments with different deposition temperatures in the range 1120 to 1320°C at an \(S_c\) of 1.9% and a 1 h deposition time were performed. For deposition temperatures above \(\approx 1225°C\), the samples have the same characteristics as described above, with nicely formed \{113\} facets. For temperatures below \(\approx 1225°C\), no \{113\} facets can be observed, but a curved band has appeared on the rim of the cylinder between the \{100\} and \{111\} facets. This band consists of high macrosteps parallel to the \{011\} PBC. In the direction of the PBC the band is flat, from which it is deduced that all \(\langle hkk \rangle_{h \geq k}\) orientations in the \{01\(\overline{1}\)\} zone, between and including \{100\} and \{111\}, are present here. The occurrence of this \(S\) zone strongly confirms the stabilizing effect of the \{1\(\overline{1}\)0\} PBCs [7], as mentioned in the foregoing description of silicon. The crystal deposited at 1225 ± 20°C has an interme-

![Fig. 3. SEM micrographs of single crystal diamonds deposited in 2.5 h at 1120°C (a, b), and in 1 h at 1320°C (c, d), both with \(S_c = 1.9\%\). Pictures (a) and (c) look down on the (100) face at an angle of \(= 20°\) with respect to the [110] direction. Pictures (b) and (d) show the \{01\(\overline{1}\)\} zone between the (111) and (100) faces, looking approximately in the [3\(\overline{1}\)1] direction. Corresponding micrographs have the same magnification.](image-url)
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diate structure, with small \{113\} facets forming a part of a curved band.

The interpretation of these experiments in terms of the stability of the \{113\} faces and the chemical roughening temperature is, however, complicated by the fact that the layers deposited on different samples do not have the same thickness. In the temperature range investigated, the growth rate in the \langle 110 \rangle \) directions increases with approximately 30 \(\mu m/h\) for every 100°C increase in the deposition temperature. The layers deposited on the rim of the cylinder are roughly 30 \(\mu m\) thick for the lowest deposition temperatures and = 65 \(\mu m\) thick for the highest temperatures. In determining these layer thicknesses it is assumed that the growth rate of all other faces behaves similarly as a function of the temperature as the growth rate of the \{110\}. The relatively thin layers, deposited at low temperatures, in combination with the small differences in the growth rates for faces in the \{011\} zone, could prevent the development of well-shaped F faces and thus obscure the determination of the chemical roughening temperature. For this reason the two experiments at the extremes of the temperature range have been repeated in such a manner that the total layer thickness deposited on both samples was the same, by changing the deposition time.

The results for the low temperature sample \(T_{\text{dep}} = 1120^\circ\text{C}, \text{time} = 2.5 \, h\) and the high temperature sample \(T_{\text{dep}} = 1320^\circ\text{C}, \text{time} = 1 \, h\) are shown in fig. 3. The layer thickness of the \{110\} face is 135 ± 5 \(\mu m\) for both samples. Although the layer deposited on the rim of the cylinder is much thicker now (= 65 \(\mu m\)), still a curved S zone is present on the low temperature sample. The angle enclosed by this band is quite large \((28^\circ ± 4^\circ)\), compared to the previously observed value for the \{113\} faces, and only a factor of two lower than the original curvature of the seed crystal \((\text{enclosed angle} \, 48^\circ ± 2^\circ)\). The high temperature sample shows nicely shaped, flat \{113\} facets. Obviously the complication of the determination of the chemical roughening temperature by the variation in layer thickness was not as dramatic as expected. However, another complication exists. Two new facets appear on the low temperature sample, which are indicated by the arrows (1 and 2) in fig. 3b. It is rather difficult to identify the exact orientations of these facets, but from their position on the crystal it follows that facets 1 and 2 must be very close to the \{113\} and \{311\} faces, respectively. If this interpretation is correct, it would mean that the chemical roughening temperature is not the same for all \{113\} faces on this crystal, which would be in conflict with the \(m_3m\) point group of diamond. However, small variations in the deposition conditions for the faces located at different positions on the same crystal might account for this phenomenon. Another possible solution to this discrepancy are in the laser grooves of the seed crystal, which are roughly parallel (after tilting towards the \{110\}) to the \{011\} PBC. This could facilitate the formation of high macrosteps consisting of small \{100\} and \{111\} faces for deposition conditions at which the surface tension of the \{311\} face and its surrounding faces is very similar to each other. These macrosteps could then obscure the \{311\} face. This reasoning is confirmed by the absence of a flat \{113\} face (indicated by A in fig. 3b) in the \{110\} zone. This area also shows high macrosteps. On the other hand, some unexplained discrepancy remains as no \{113\} or \{311\} faces are present on the high temperature samples where the \{311\} face is much more stable. It should be mentioned that the transition from an F to an S face observed in silicon CVD was also rather gradually, with an intermediate morphology having hardly detectable \{113\} faces [9].

Two more, interesting observations can be made about the crystal grown at low temperatures. Firstly, there exist regions around the \{101\} and \{110\} orientations, indicated by arrows (3 and 4) in fig. 3b, which have the same pitted structure as the \{110\} face. Probably the pitted structure stabilizes these faces. This gives some evidence to the idea that the wall of the pits have orientations corresponding to stable F faces. In the \{101\} region it can be observed that the original grooves of the seed crystal still prevail in the final structure. Secondly, very large growth hillocks crossing the full width of the facets are present on the \{111\} and \{111\} faces, as indicated by the arrows in fig. 3a. Remarkably the step directions of slow-
est growth corresponding to these hillocks, \{\overline{1}1\overline{2}\}, are inverted with respect to the steps normally present on \{111\} diamond. This can be explained by the occurrence of step reconstruction [22].

From our experiments we deduce that the chemical roughening temperature for the \{113\} faces of flame grown diamond lies around \(1200 \pm 100^\circ\)C. The uncertainty is estimated from comparing the crystal in fig. 1 with the crystals in the temperature series and from the discrepancy in the formation of different \{113\} faces on the same crystal. Of course, the temperature above which \{113\} facets start to appear is not only dependent on the deposition temperature but also on the other growth conditions such as the input gas composition and the position of the seed crystal in the flame. A more elaborate study seems worthwhile, on the condition that better types of substrates – either hemispheres or cylinders with smooth walls – are used.

4. Conclusion

In conclusion we have shown for the first time that, apart from the well-known \{111\} and \{100\} faces, also \{113\} facets can be formed on diamond by CVD techniques. These \{113\} facets and their relative stability have originally been predicted by a crystal growth theory developed for silicon CVD. The described experiments show that the influence of surface reconstruction and surface coverage on the crystal growth described by this theory apply also to the deposition of diamond, at least in a qualitative way. A quantitative correlation between the experimental results and the theoretical model would require detailed knowledge – either experimental or theoretical – about the composition of the gas phase at the growing crystal, in order to find the surface coverage of the diamond. The observation that a theory derived under the assumption of near-equilibrium growth conditions applies so well to our experiments is somewhat surprising. Two conflicting conclusions are possible: (1) The theory could be valid for a much wider range of conditions, even for the CVD of diamond which is generally assumed to be a far from equilibrium process. (2) Much more fascinating would be the conclusion that diamond deposition is a near-equilibrium process at the growth conditions used in this study. In a forthcoming paper a more elaborate theoretical and experimental comparison between diamond and silicon deposition will be made [14].

Acknowledgements

The authors wish to thank Mr. G.C.J. Otter and Ing. W. Vollenberg for their technical assistance. The diamond workers at Drukker International BV, Netherlands, are thanked for the preparation of the diamond seeds. This work was performed as part of the research program of the Netherlands Technology Foundation (STW) with financial support from the Netherlands Organization for Scientific Research (NWO).

References