Surface stabilization phenomena on flame-deposited diamond single crystals

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Abstract

The acetylene-oxygen combustion flame technique was applied to the homoepitaxial deposition of diamond single crystals on cylindrically shaped \{111\}, \{001\} and \{110\} type IIa natural diamond substrates. After deposition the specimen revealed surface stabilization phenomena like flat facets and curved bands for orientations corresponding to Miller indices \(\langle hkk \rangle_{h<k}\) in the \langle110\rangle zones. The surfaces of all other orientations have a rough appearance, because they are stabilized by the development of microfacets which also have orientations close to \(\langle hkk \rangle_{h<k}\). The observed phenomena can be explained by a broken bond analysis of the diamond crystal with additional considerations about surface reconstruction by dimer formation.

1. Introduction

The technique of growing diamond from a highly activated gas phase mixture of hydrocarbons and relatively large amounts of hydrogen was known for more than 25 years in the former Soviet Union [1,2]. Since Japanese scientists confirmed diamond growth by this technique in 1982 [3], a still increasing number of research groups is investigating the formation of diamond by chemical vapour deposition (CVD). At this moment the major application of the material is for thermal management purposes. Expected applications in the future are protective coatings, optical coatings, windows and semiconductor electronic devices [4]. Especially for the latter applications growth of single crystalline layers is desired. Unfortunately the use of cheap substrates, like silicon or molybdenum, leads to the deposition of polycrystalline films. Therefore in recent years homoepitaxial growth on natural or high pressure/high temperature synthesized diamond substrates has gained more and more interest [4,5]. In 1988 Hirose and Kondo [6] reported diamond growth from an acetylene-oxygen oxygen combustion flame using a commercially available welding torch. It appeared that, over a limited deposition area, very good quality diamond films can be obtained at high deposition rates. These features make the combustion flame an excellent technique for growth on single crystal diamond substrates, which up until now are only available in rather limited dimensions [5,7,8]. In the present study the occurrence of facets and other forms of surface stabilization on such flame-deposited diamond single crystals is described.

2. Experimental procedure

Cylindrically shaped, natural type IIa diamonds, 0.25 mm thick and 2 or 3 mm in diameter, with \{111\}, \{001\} or \{110\} top and bottom faces were used.
as substrates. The \{111\} substrates obtained by cleavage, were, apart from the cleavage steps, exact in orientation, whereas the others were polished to within 3° of the exact orientation. During growth the seed crystals were placed in the centre of an acetylene feather obtained from an acetylene–oxygen combustion torch using a gas mixture with an excess of 3 to 5% of acetylene compared to the neutral flame [9]. The distance between the crystals and the flame front, which is the activation zone of the gas phase, ranged between 0.8 and 1.5 mm, while the total flow of the source gasses was about 6 standard litre per minute. The deposition temperature was kept constant at values between 1100 and 1250°C, using an in-house developed cooling system [9].

After growth the specimens were investigated by optical differential interference contrast microscopy (DICM) and scanning electron microscopy (SEM). The orientations of the facets developed along the sides of the samples were determined with the help of a two-circle optical reflection goniometer. Depending on the top face orientation of the substrate used, the specimens discussed in this study will be referred to as \{111\}, \{001\} or \{110\} samples.

3. Results

Besides the \{111\} and \{001\} facets, which are commonly encountered on CVD diamond [2,7–10], the samples examined in this study reveal a number of additional surface stabilization phenomena. Around the sides of the cylindrically shaped \{111\} samples, which are regions of relatively low curvature (radius > 1 mm), curved bands with macrosteps and more or less planar features have developed (see Figs. 1a and 1b). The orientations of these bands correspond to the \{hhk\}_{h<k} parts of the \{110\} zones between the \{111\} and the \{001\} side facets. Fig. 1b shows a DICM image of such a band which exhibits a high density of macrosteps in the region close to the \{111\} face and flattened features near \{001\}. The occurrence of these curved bands with macrosteps indicates a stabilization of the crystal surface in one direction, namely \{110\} which is along the macrosteps orthogonal to the curvature of the band. The flattened features must be due to a stabilization of the surfaces in one or more directions, additional to \{110\}. Apparently the increased stabilization of the flattened areas in the direction orthogonal to the macrosteps, is not sufficient to develop discrete planar facets. Therefore these regions are best described as F faces just above the roughening temperature [11].

Because of mutual competition, the most stable, i.e. the slowest growing orientations, determine the morphology in regions of higher curvature. Such regions with a radius < 0.2 mm exist in the six \{110\} zones which run from top to bottom along the sides of the – including the seed crystal – less than 0.3 mm thick \{111\} samples (see Fig. 1a). In these zones a sequence of broad, connected facets have developed which have a different appearance for the two symmetrically non-equivalent sets of three. Figs. 1c and 1d show an example of each set which will be referred to as type I and type II respectively. Without differences in the local growth conditions at the surfaces, the appearance of set II from bottom to top would be identical to that of set I from top to bottom. However, the gas phase, which is highly activated at the flame front of the combustion flame, is transported towards the substrate by a forced flow. During transport the composition of the gas phase changes due to chemical reactions between the various gaseous species. This introduces a difference in the growth conditions between the top and the bottom of the samples, which causes the observed differences between both types of faceted sets. The facets near the bottom of the specimen are especially ill-defined since they have angles of more than 90° with the top face and did not directly face the main gas flow during growth. From the surface topographs it is clear that in the \{hhk\}_{h<k} parts of the \{110\} zone between two octahedral faces no additional faces are formed. On the other hand, in the \{hhk\}_{h<k} parts of the \{110\} zones additional faces have appeared besides the commonly observed \{001\} facets. In the type I sets these are identified as \{112\}, while in the type II sets they are denoted as \{11X\} with 3 < X < 7, because they are still slightly curved and give a diffuse reflection or a band of reflections in the optical goniometer. The \{112\} facets of which the morphological importance in most cases is quite low (see Fig. 1c), make an angle of 90° with the top face of the sample and are probably just the “translated” sides of the substrate. They have not yet disappeared.
from the final crystal form, but have broadened at the expense of the rough faces on both sides of the \( \langle 110 \rangle \) zone. In the type II sets the \( \{112\} \) faces are already disappeared, due to the development of neighbouring \( \{11X\} \) faces which more directly face the main gas flow and are not shielded like the \( \{11X\} \) orientations in the sets of type I. For a \( \{111\} \) specimen with, as a result of a higher deposition temperature, a thicker epitaxial layer than the sample shown in Fig. 1, the \( \{112\} \) faces do not occur. Despite being shielded from the gas flow, the \( \{11X\} \) faces were formed at the bottom half of this sample in the type I sets. At the same sample the morphological importance of the \( \{11X\} \) faces with respect to the \( \{111\} \) and \( \{100\} \) has increased. Several of them reveal a rim indicating the formation of two different faces \( \{11X_1\} \) and \( \{11X_2\} \) \( 3 < X_1, X_2 < 7 \) as is shown in Fig. 2a.

The \( \{001\} \) and \( \{110\} \) samples could be deposited at a higher supersaturation of 4 to 5%, instead of the 3% used for the octahedral specimen, because these surfaces suffer less from the occurrence of stacking faults and twin formation. This resulted in higher growth rates and epitaxial layers exceeding 100 \( \mu \)m in thickness, which allowed the examination of the more mature stages of the features observed on the less than 60 \( \mu \)m thick \( \{111\} \) specimen. Apart from the top faces of the \( \{110\} \) samples, the cubic and dodecahedral specimens reveal hardly any rough surfaces, but are completely bounded by flat \( \{111\} \) and \( \{001\} \) facets. In most cases they also reveal flat \( \{113\} \) facets [12] (see Fig. 2b), from which it can be

![Fig. 1. Schematic drawing and compositions of DICM photographs revealing surface stabilization phenomena in the \( \langle hhk \rangle_{<4} \) parts of the \( \langle 110 \rangle \) zones of a single crystal diamond layer grown on a cylindrically shaped \( \{111\} \) natural diamond substrate \( \left( T_d = 1150^\circ C, S_m = 3\% \right) \). (a) Schematic drawing of the sample indicating the positions of the curved bands and faceted sets shown in (b), (c) and (d). (b) Curved band with macrosteps and flattened areas in a region of low curvature between I and II. A type I (c) and a type II (d) set of connected facets in regions of higher curvature running from top to bottom of the sample.](image-url)
other rough surfaces observed on flame grown single crystals. Close inspection of these dodecahedral faces by SEM reveals that this structure consists of micrometre sized facets of different orientations (see Fig. 2c). The average orientations of these microfacets were determined by laser reflectometry using the 632.8 nm line of a He–Ne laser. Using this technique the orientations can be calculated from the angular distributions of the back reflections of a parallel laser beam incident perpendicular to the crystal surface. The measurements show that the orientations of the microfacets on the rough surfaces have orientations close to \( \{hhk\}_{h<k} \) [7]. The measured orientations show a slight discrepancy with the \( \{hhk\}_{h<k} \) parts of the \( \langle 110 \rangle \) zones, because the microfacets are not fully developed but are somewhat rounded. The rounded shape of the facets can be explained by the fact that the re-entrant corners between the microfacets in the pits are preferred nucleation sites for steps, resulting in the concave shape of the facets. Due to the development of the microfacets the total surface area has increased with respect to the flat \( \langle 110 \rangle \) surface of the seed crystal. Because the surface develops towards a minimum energy configuration, the surface free energy of the microfacets must be less than that of the orientations on which they have developed so that a net gain in surface free energy is obtained despite an increase in surface area.

Fig. 2. SEM details observed on several flame-deposited diamond single crystals. (a) Side view of one of the type II sets on a \{111\} sample taken at an angle of \( \sim 55^\circ \) with respect to the top face revealing a rim (see arrow) indicating the splitting of a \( \{11X\} \) face into two separated faces \( (T_d = 1250^\circ C, S_{ac} = 3\%) \). Note that the small face above the \( \{11X\} \) face is a \( \{113\} \) facet and that the \{001\} face does not occur in the type II set of this sample. (b) Perpendicular view on a flat \{311\} facet on a \{001\} sample \( (T_d = 1150^\circ C, S_{ac} = 4\%) \). The facet is located at the periphery with the top face and is bounded by \( \{100\} \) and \{111\} facets at the left respectively right hand side. (c) A pattern of microfacets on the top face of a \{110\} sample taken at an angle of \( \sim 55^\circ \) \( (T_d = 1200^\circ C, S_{ac} = 4.5\%) \).

concluded that this is the final form of most \( \{11X\} \) faces observed on the \{111\} samples. The top faces of the \{110\} samples have a pitted structure like all

4. Discussion

According to the periodic bond chain (PBC) theory (flat) F faces occur for orientations \{hkl\} with two or more interconnected chains of strong bonds (PBCs) within the repeat distance \( d_{hkl} \) [13]. These faces appear as planar facets on the crystals. For a continuous set of (stepped) S faces, which have PBCs in only one direction within \( d_{hkl} \), a growth band which is flat along the PBCs but curved in the perpendicular direction is expected to develop. Orientations without PBCs within their repeat distance are kinked (K faces). Such faces have no tendency to flatten and appear as rough surfaces. For diamond the only PBC is the zigzag carbon chain of covalent, nearest neighbour bonds parallel to \( \langle 110 \rangle \). From this it follows that the only F faces are \{111\}, the \( \{hhk\}_{h<k} \)
parts of the \((110)\) zone are S-type and the remaining orientations, including \(\{hhk\}_{h \geq k}\), are kinked [14].

The specimens described in the present study indeed reveal \(\{111\}\) facets. The \(\{hhk\}_{h \geq k}\) orientations, however, all have a rough appearance. This indicates that, under the applied growth conditions, the presence of \(\langle 110 \rangle\) PBCs in only one direction is not sufficient to give any kind of surface stabilization. Furthermore, in contrast to the results of the first order broken bond PBC analysis of the diamond structure, curved bands and flat facets were observed in the \(\{hhk\}_{h \geq k}\) parts of the \(\langle 110 \rangle\) zones. The presence of flat \(\{001\}\) facets in this zone is explained by a \((2 \times 1)\) surface reconstruction due to the formation of dimer bonds, by which the dangling bond density at the surface might be reduced by as much as 50\% [15]. Upon this reconstruction the surface free energy is lowered and a positive step free energy is created, resulting in layer by layer growth and the development of an F face. Similar to \(\{001\}\), the surface atoms of the other \(\{hhk\}_{h < k}\) orientations are also capable of dimer formation. Recently the maximum reduction in dangling bond density, which can be obtained according to different geometries of these dimer bonds on these surfaces was considered in detail [16]. The results of this theoretical study are summarized in Fig. 3. It is clear that each configuration reduces the dangling bond density of the \(\{hhk\}_{h < k}\) orientations, but in particular the configuration \(R_\perp\) with the dimers perpendicular to the \(\langle 110 \rangle\) PBCs contributes to the stabilization of the surface in two directions, by the formation of a connected net of strong bonds [17]. Due to the decrease in dangling bond density, these surfaces have a lower surface free energy (and kinetic coefficients) than the neighbouring orientations outside the \(\langle 110 \rangle\) zone, so they obtain an S face character. Furthermore, due to \(R_\parallel\) a discrete number of orientations between \(\{113\}\) and \(\{001\}\) can reduce their dangling bond density with respect to all their neighbouring orientations, including those in the \(\langle 110 \rangle\) zone and therefore might appear as flat facets. In practice all possible dimer geometries as well as some non-reconstructed regions are expected to coexist. Therefore only the orientations corresponding to the most pronounced minima according to \(R_\parallel\) and possibly also the \(\{115\}\) according to the hybrid geometry (see Fig. 3), might be subject to stabilization in two directions and thus appear as planar facets [16].

In addition to dimer formation the adsorption of species from the gas phase on the surface may account for stabilization of certain crystal faces by the creation of extra surface PBCs, but also for destabilization due to chemical roughening [11]. Recently it became clear that the surface morphology of several crystal faces on flame grown single crystals is largely influenced by the presence of nitrogen containing species in the gas phase during growth [18,19]. To what extent these species, which in the case of flame deposition originate from in-diffusion of nitrogen from the ambient, also influence the stabilisation of the \(\{hhk\}_{h < k}\) orientations is subject of future investigations.

5. Conclusions

The facets and curved bands with macrosteps on the flame grown diamond single crystals described in this study only occur in the \(\{hhk\}_{h \leq k}\) parts of the \(\langle 110 \rangle\) zone. In this zone the \(\{111\}\), \(\{001\}\) and under certain conditions also the \(\{113\}\) orientations appear as flat facets. Curved bands with pronounced macrosteps between \(\{111\}\) and \(\{113\}\) indicate that these orientations are stabilized in one direction,
while the flattened areas between \{113\} and \{001\} indicate a more two dimensional stabilization. The observed phenomena can be explained very well by making the assumption that, for orientations with Miller indices \{hhk\}_{h,k}, besides the \{110\} PBCs, additional surface PBCs are created by the formation of dimers in several geometries.

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