On a characteristic misorientation structure within (001) facets of CVD-grown diamond crystallites: an analysis by optical microtopography, interferometry, electron diffraction and cathodoluminescence

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Certain crystallite populations in microwave plasma CVD-grown diamond films contain large octahedral grains oriented with [001] normal to the film and topped by (001) facets several tens of micrometres in edge length. These facets show characteristic growth step patterns and related characteristic cathodoluminescence patterns. Conflict between the interpretation of step patterns and the facet surface profiles determined interferometrically required a quadrantal division of (001) facets by low-angle boundaries for its explanation. Misorientation determination by electron channelling and electron backscatter diffraction techniques confirmed this model; and partially polarized cathodoluminescence attributed to dislocations associated with the low-angle boundaries was observed. Occurrences of this misorientation texture in (001)-faceted CVD-grown crystallites, without restriction to particular growth techniques, are to be expected.

1. Introduction

A scientific surprise of recent years has been the relative ease with which substantial diamond films can be grown by chemical vapour deposition (CVD) methods. DeVries (1987), Angus & Hayman (1988) and Angus et al (1993) describe the rapid evolution of the art, following two decades of slow progress. Naturally, early work concentrated on homoepitaxial (diamond-on-diamond) growth, but the introduction of successful nucleation and growth on non-diamond substrates, such as silicon, effectively removed area limitations on film growth. Bachmann (1994) and Spitsyn (1994) review the many growth techniques now in use. One method uses a microwave-activated plasma in a H₂ + CH₄ flow system for deposition of diamond on an abraded Si monocrystal substrate (Kamo et al 1983; Sato & Kamo 1992). The material here described was grown this way. The factors controlling the orientation texture in polycrystalline diamond films, and the habits of individual crystallites, are topics of intensive investigation; good progress is being made in producing films uniform in texture and crystallite size (Wild et al 1994). The specimen involved in this study was far from uniform in crystallite size and...
orientation. It contained a proportion of relatively large octahedral crystallites, oriented with a cube axis ([001], say) normal to the film, all truncated by a large (001) facet that stood substantially higher than the summit level of surrounding smaller crystallites. These large cube facets attracted attention not just by their prominence, but by the characteristic step patterns on them, coupled with striking cathodoluminescence (CL) patterns. However, when the facet surfaces were contoured by optical interferometry the findings conflicted with a straightforward reading of the step patterns. The resolution of this conflict, achieved by bringing together evidence from optical microscopy, electron diffraction and CL, is described below.

2. Observations

(a) Crystallite morphology

The specimen was grown at the Naval Research Laboratory, Washington, DC. The gas in the reactor was H2 with 3.6% CH4 and 0.5% O2, pressure 110 Torr, and the microwave power was 5 kW. The silicon substrate temperature was not measured, but probably exceeded 1000 °C. The diamond film was studied after removal of substrate, most observations being made on a broken-off piece about 3 mm in diameter. For assessing morphologies, the film, overall thickness ca. 235 μm, was micrographed in transmission, a typical area being shown in figure 1. The considerable height difference, 20–25 μm, between the large (001) facets and the surrounding ‘undergrowth’ of small crystallites rendered it impossible to view both sharply at the same focal setting, but significant focal depth increase and improvement in light collection from undergrowth facets was achieved by viewing with di-iodo-methane, CH2I2, nD = 1.74, filling the volume between undergrowth and a cover slip lying on the (001) facets. Viewing between crossed polarizers also increased distinctness of undergrowth features in figure 1a and was necessary in figure 1b for improving the contrast of images of large grains relative to a confused background of small-grain images.

Differences in crystallite size, morphology and orientation are excellently revealed by CL colour microphotography. Figures 2a–c were obtained using the Lang & Meaden (1991) variant of the CL topographic technique: the specimen surface was viewed directly, without use of mirrors that can impair detection of polarization in CL emissions. This arrangement necessitated oblique impingement of the electron beam on the specimen, the mean grazing angle being about 20°. There is then strong dependence of brightness on local surface orientation, and upstanding objects such as the large octahedra topped by (001) facets cast shadows. Figures 2a and b illustrate typical distributions of large and small crystallites; in figure 2c the region in the top right corner of figure 1a will be recognized. As in figure 1a, focusing at the mean level of the large (001) facets sends the undergrowth out of focus, and no immersion medium can be used in the CL case. Re-focusing on the undergrowth brings out much interesting detail in the CL of small grains that is not apparent in figure 2. Salient features to note here (seen best on the original transparencies) are as follows. (1) The largest (001) facets have a pink tinge, whereas smaller (001) facets (edge length under about 30 μm)

† 1 Torr ≈ 133 Pa.

Figure 1. Transmission optical micrographs of specimen viewed between crossed polarizers, axes vertical and horizontal. Field width 0.87 μm. (a) Focus at mean level of (001) facets. The largest crystallite in the field, seen near top right corner and having facet edges vertical and horizontal, will be referred to as 'grain A'. (b) Focus adjustment 51 μm below (a), equivalent to 123 μm lower within diamond (refractive index 2.42).

appear entirely orange-yellow. (2) The CL pattern on the largest (001) facets is 4-fold symmetric, describable in simplified terms as being divided into quadrants by a narrow violet-blue cross, with orange-yellow emission bright near facet corners, and between cross and corners unsaturated blue and/or pink colours are seen. (3) In the undergrowth, octahedral facets emit blue-green, but all upward-pointing octahedron vertices emit bright orange-yellow (possibly from small (001) facets). Size measurements of 180 crystallites conspicuous by exhibiting feature (1) and at least some development of feature (2) gave 44 μm as their average (001) facet edge length in this specimen.

From higher-magnification transmission optical micrographs, such as figure 3, which shows grain A (pointed out in figure 1) and its companions, the distances
Figure 2. For description see opposite.

from (001) facet to bottom octahedral apex of some of the largest crystallites were measured. (Dimensions of grain A are discussed in §3.) It was verified that the sloping surfaces surrounding the (001) facets were {111} facets, but they were very rough. Bottom apices of large octahedra, their 'roots', can be located by viewing either from above, through the (001) facets, or from below, through the rough lower surface of the film. Measurements of root depth made from these two surfaces were in rough concordance. Birefringence suggests a concentration of stress near the roots that has general radial symmetry about [001]. The patterns seen when specimen and crossed polarizers are mutually rotated about [001], and focus is at root level, are superimpositions of the geometrical image of the bottom apical region upon an extinction cross parallel to the axes of the crossed polarizers that rotates with them (figures 3c and d).

(b) Surface topography and lattice misorientation

The majority of large (001) facets are tilted not more than about 2° off the plane of the film, and show surface steps. With few exceptions (such as interference by neighbours) facets greater than ca. 25 μm in edge length have step patterns exhibiting some degree of four-fold symmetry, which becomes more evident on larger facets. Figure 4 shows examples: (a) is grain A, (b) is a grain nearer average size, and (c) and (d) show a grain whose surface is bisected by a fracture outcrop. (About one in seven of facets greater than 40 μm in edge length have shallow fractures.) Many such step patterns, composed of central astroids surrounded by rectangular hyperbolae (roughly), are so alike that reference to

Figure 4. Nomarski differential interference contrast micrographs of (001) facets, magnification ×10³. In (a), (b) and (c), the conventional shadowing direction simulating illumination from upper left applies; in (d) illumination downwards is simulated, to render the crack step almost invisible.

Adjacent landmarks is needed to avoid confusing the identity of the crystallites exhibiting them. Maximum step heights are between 10 and 20 nm, and step spacings lie between 3 and 5 μm on average, both independent of facet size. The step risers tend to lack continuity, often disappearing into a surface apparently undulating on a height scale of a few nanometres, the resultant of small steps on or below the microscope resolution limit.

With steps facing inwards from corners it is natural to infer that the corners
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Figure 5. Two-beam interferograms of (001) facet of grain A. (a) Fringes set diagonally to show the gull-wing pattern: displacement of fringe locus towards the lower left corner represents increase in surface level. (b), (c) Reference mirror nearly parallel to mean plane of summits in the four quadrants. In (b) these summits are touched by a bright fringe, the surrounding dark fringe contouring a lower level. In (c) the specimen has been raised so that the 'four-leaved clover' dark fringe has expanded, but still partly embraces the central dip.

stand highest on the facet. However, contour mapping by a Michelson interferometer attached to the microscope tells a different story. Due to the range of facet tilts present, observing the facet population with a fixed reference-mirror tilt produces fringe patterns varying widely in fringe direction and spacing. Conspicuous among these patterns is prevalence of a 'sea-gull wing' trajectory of fringes crossing individual facets, indicating a dip at the centre of the astroid step pattern, as expected, but also a definite camber towards facet corners that can bring them below the level of the central dip. Figure 5 shows two-beam fringe patterns on grain A. Because a small illuminating aperture is used, step edges show up quite strongly as phase contrast images. These relatively sharp edge images should not be confused with surface contours, and are useful for matching interferograms with Nomarski patterns (cf. figures 4a and 5). For contour analysis colour photographs were most effective, and were used to derive the profiles discussed in §3.

Rejecting as too improbable the notion that the mean outward surface slope in each quadrant is built up from saw-tooth segments oppositely sloping relative to underlying (001) lattice planes constant in orientation over the whole facet, it is necessary to invoke different lattice orientations in each quadrant. Specifically, the [001] direction in each quadrant must have a tilt component outwards towards its facet corner not less than the mean surface camber slope at the corner in order to produce step patterns as in figure 4. The electron channelling pattern (ECP) technique (Coates 1967; Booker 1970) has very appropriate angular and spatial resolutions for the misorientation mapping needed to verify this hypothesis. It was carefully applied to grain A and revealed misorientations of the magnitude and direction predicted (figure 9, discussed in §3). Misorientations across some other large (001) facets were examined with higher spatial resolution using the electron backscatter diffraction technique (Dingley & Randle 1992), but permanent records were not taken. However, real-time observations confirmed outward splay angles of 1–2° between [001] axes in opposite quadrants. Orientation changes were abrupt in the vicinity of quadrant boundaries, indicating presence of low-angle boundaries there.

(a) Monochrome record of full visual-spectrum CL from region including grain A. (b), (c) Images recorded through blue-passing Ilford filter 304 (transmission greater than 1% between 385 and 500 nm, roughly) and a linear polarizing filter. (b) E-vector horizontal. (c) E-vector vertical.

(c) Dislocation cathodoluminescence

Many spatially localized CL emissions have been recorded from CVD diamond films of the present and other types, and will be reported elsewhere (Burton et al 1995). Of immediate interest here is the violet-blue cross seen on (001) facets in figure 2. However, one other CL feature deserves a remark. The pink tinge on large (001) facets is attributable to the 2.16 eV, 575 nm vibronic system. Several topographic associations of this system in natural diamond have been described (Hanley et al. 1977). It is also a strong component in CL from polycrystalline synthetic diamond compacts (Collins & Robertson 1985): note similarities between the colour image, plate 2b, in Lang et al (1992), and figure 2 here. In natural and synthetic diamonds low in nitrogen impurity, and consequently free from dominance of their CL by nitrogen-related defects, individual dislocation lines show up by violet-blue CL strongly polarized with E-vector parallel to the dislocation line (Kiflawi & Lang 1976; Hanley et al 1977). The violet-blue emission from the crosses that divide (001) facets into quadrants visually resembles dislocation CL, is partially polarized, and is largely attributed to dislocations in and near the low-angle boundaries that misorientation measurements require. As explained in § 3, tidy alignment of dislocations in ideal planar boundaries is not expected in the present case, so only modest dominance of CL with E-vector parallel relative to that with E-vector normal to cross arms, as demonstrated in figure 6, is understandable. The crystallites imaged can be recognized in the full-spectrum CL topograph, figure 6a; images (b) and (c) select the violet-blue emission. (In these and other CL topographs disregard excess brightness issuing from edges between (001) and adjacent octahedral facets that face the electron beam: it arises largely from escape of internally trapped light.) In grain A the relatively stronger polarization in the horizontal arm of the cross is consistent with the relative narrowness of its image seen in figure 2c. The large crystallite cut by the upper left margin of the photographs shows little difference between (b) and (c) because its cross arms are rotated about 33° clockwise from horizontal and vertical. Easily observable differences between (b) and (c) images are shown by the crystallite near the bottom right corner, and especially by the smaller crystallite at centre bottom in the field.
3. Interpretation

Figures 7–9 present data derived from measurements described in §2. Figure 7 shows the scale of the largest crystallites relative to the overall film thickness; the actual dimensions relate to grain A. Uncertainties of about 5 μm attach to distances FR, BR and the overall thickness FB. The wide girdle region of the octahedron cannot be seen through the (001) facet, and its section is surmised from knowledge of the mean (001) facet width, 71 μm, and the depth FR. The nucleation of large octahedra having cube axes normal to the film after about 80 μm thickness of film had already grown probably occurred in response to a film temperature change (but is undocumented).

The surface profiles in figure 8 disregard individual steps since a single step, even the largest, represents a small fraction of the total relief. The well-developed four-fold symmetry of surface topography on the two crystallites concerned justifies taking an average centre-to-corner profile in each case. Regarding grain A, the mean camber inclination in an outward diagonal direction at corners of the (001) facet is about 0.3°. The rough constancy of step spacings over most of the

facets suggests that the diagonally outward lattice tilts at corners should be not less than about twice this angle. Results of the misorientation determination by ECP are plotted in figure 9, and show actual diagonally outward tilts comfortably exceeding the camber slope. Errors in orientation difference measurements are believed to be within $\pm 0.2^\circ$.

The findings illustrated in figures 8 and 9 are combined in figure 10, a schematic vertical cross-section through the facet surface and volume immediately below it, taken along a facet diagonal, and shown with exaggerated vertical scale. Outward lattice tilts in the opposite quadrants are drawn equal and opposite, for simplicity. (Figure 9 showed mutual tilts between opposite quadrants to be the same for both diagonals, 1.8$^\circ$, within the accuracy of measurement.)

Turn now to an explanation of the systematic misorientations observed. Manifestations of the CL ‘blue-cross’ feature are recognizable on facets down to edge lengths of ca. 25 $\mu$m. Nomarski micrographs show good development of step patterns like those of figure 4 on facets of edge length 25 $\mu$m, and patterns interpreted as their incipient development on facets down to ca. 15 $\mu$m in edge length. Lack of obvious dependence on facet size of step heights and spacings on the present specimen has been noted in §2a. Taking a uniformitarian approach (in absence of contrary evidence) suggests that the larger facets developed their present type of step pattern when their edge lengths were not greater than 25 $\mu$m. Spreading of growth layers from facet corners inwards involves the meeting of oppositely moving growth steps along junctions whose mean loci will form a cross dividing the facet into roughly equal quadrants. This coming together of growth steps
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is highly likely to trap non-diamond structures (e.g. methyl groups) at feet or on risers of steps, and in consequence build in edge dislocations parallel to the junction: dislocations lying along [110] with Burgers vector direction [110], and lying along [110] with BV direction [110]. Loci of successive step junctions can be expected to sway back and forth somewhat across adjacent quadrant boundaries during growth, and the step patterns bear evidence of this. Hence the grown-in dislocations will be distributed in bands parallel to quadrant boundaries, the band width corresponding to the spatial width of the arms of the violet-blue cross. To accommodate the lattice misorientations generated at quadrant boundaries parallel to both [110] and [110], such boundaries will become half tilt, half twist in character, producing diagonally directed resultant misorientations, as observed. It is predicted that misorientation structures similar to those described here will be observed in other (001)-faceted CVD diamond crystallites, independent of growth technique, provided that growth on such facets has progressed by inward motion of macrosteps resulting from independent growth layer nucleation at facet corners.

An explanation of the cracks seen on (001) facets can also be advanced. These cracks show up brightly in CL topographs by the light they scatter. Most common are single cracks, roughly bisecting facets, but a few examples of T-shaped crack outcrops along three of the four quadrant boundaries appear. Crack plane orientations are roughly \{111\}. All are shallow. The 13 µm depth of crack tip below facet surface measured in the crystallite shown in figure 4c, d is typical (and occurrence of growth steps crossing the crack confirms the latter as being a post-growth event). Now although the half tilt, half twist low-angle boundaries require growing-in of some dislocations with trajectory components normal to the facet, the majority will be grown in lying parallel to the facet. Perpetuation of a given misorientation requires fresh generation of such dislocations at a constant rate. If during final stages of growth on (001) facets in this specimen the degree of incorporation of non-diamond structures at step junctions declined, then the required dislocation rate would not be met, and surface layers would be placed under tensile stress.

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References

Burton, N. C., Steeds, J. W., Meaden, G. & Butler, J. E. 1995 Diamond Related Mater. (Submitted.)


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