Effect of off-axis growth on dislocations in CVD diamond grown on {001} substrates

Nick Davies\textsuperscript{1,3}, Riz Khan\textsuperscript{1}, Philip Martineau\textsuperscript{1}, Mike Gaukroger\textsuperscript{1}, Daniel Twitchen\textsuperscript{2} and Harpreet Dhillon\textsuperscript{2}

\textsuperscript{1}DTC Research Centre, Belmont Road, Maidenhead, Berkshire, SL6 6JW, UK
\textsuperscript{2}Element Six, King’s Ride Park, Ascot, Berkshire, SL5 8BP, UK
\textsuperscript{3}Author to whom any correspondence should be addressed.

Email: nick.davies@dtc.com

Abstract. Single crystal CVD synthetic diamond samples grown on substrates close to (001) have been studied using X-ray topography, photoluminescence imaging and Nomarski microscopy. The substrates used for this study were polished up to 15 degrees from (001). Nomarski images of the final growth surface have been compared with X-ray section topographs and photoluminescence images, both sampling a plane close to the surface of a (010) cross-sectional slice. The photoluminescence images provide evidence of the direction of step flow growth which was compared with the surface morphology. Samples grown on substrates polished off-(001) about [010] by greater than 10 degrees exhibit regions possessing both [001] and [101] dislocations as a result of on-axis and off-axis step flow growth respectively. Our previously published model suggests relatively low angle surface inclinations arising from risers are needed to switch dislocation direction from [001] to [101] line direction, and core energies per unit length suggest a minimum riser angle of 10 degrees is required. Samples grown on substrates polished greater than 10 degrees from (001) exhibit dislocations with a [101] line direction consistent with the model. Below this angle the dislocations do not switch line direction. Possible mechanisms influencing dislocation line direction via off-axis growth are discussed.

1. Introduction

There is currently much interest in the use of single crystal chemical vapour deposition (CVD) synthetic diamond in applications which make use of its exceptional optical, thermal, electronic and/or mechanical properties. While point defects in single crystal CVD diamond have been studied for many years [1], relatively little has been reported on the extended defect content of this material and how these may be influenced via the control of growth parameters. Extended defects, such as dislocations and stacking faults, are likely to influence the suitability for applications such as electronic devices. Extended defects are also known to affect the birefringence of diamond material [2] as a result of the associated strain; this is likely to be significant in optical applications such as laser windows, lenses and Raman lasers.

Comparing different diamond types, natural type IIa diamond contains relatively high dislocation densities (up to $10^9 \text{ cm}^{-2}$) [3] resulting from plastic deformation. These are arranged either in slip bands or in networks resulting from polygonisation [2, 4]. In contrast, dislocations in single crystal CVD diamond material tend to nucleate at or near the interface with the substrate on which it is
homoepitaxially grown and possess line directions close to perpendicular to the local growth surface. Birefringence and X-ray topography can be used to study these dislocation configurations and their variation from sample to sample [2]. Gaukroger et al [5] used X-ray projection topography to analyse the Burgers vectors of dislocations in samples of single crystal CVD diamond grown on (001) substrates. Two types of dislocation with line directions close to the [001] growth direction were identified. Mixed 45º [001] dislocations were found to be associated with damage at the substrate surface. Clusters of four or more edge [001] dislocations emanating from points at the substrate surface were also identified. Fujita et al. [6, 7] have presented the results of ab initio modelling of both edge and mixed <001> dislocations, and Blumenau et al. [8, 9] have reported the results of ab initio calculations for 60º and screw dislocations and an investigation of their dissociation. The core energy per unit length for these different dislocation types has been used by Martineau et al. [10] to calculate a minimum surface inclination angle (e.g. riser angle) with respect to dislocation line direction above which the dislocation line direction changes from [001] to [101]. In this paper we further test this hypothesis and report growth on substrates miscut from the {001} direction.

2. Experimental details

2.1. CVD diamond samples
The homoepitaxial diamond samples studied here were grown by Element Six Ltd. using microwave plasma CVD on {001} type Ib CVD diamond substrates possessing either (010) or (110) side faces processed into parallel-sided plates. The samples investigated were all standard CVD synthetic diamond similar to those in previous publications [2, 10]. The substrates were polished between 4º and 15º from [001] about [010] in order to investigate the effect of off-axis growth on the dislocations. Table 1 lists details of the samples discussed in this paper.

Table 1. Sample details.

| Sample | Substrate preparation |
|--------|-----------------------|
| A      | Polished 4º from [001] about [010] |
| B      | Polished 15º from [001] about [010] |
| C      | Polished 10º from [001] about [010] |

2.2. Luminescence imaging
Photoluminescence images were recorded using a DiamondView instrument that exposes samples to above band gap UV radiation to excite surface luminescence and can give information about spatial variations in the intensity of luminescence emanating from point defects or dislocations. After X-ray topography analysis {001} polished cross-sections were processed from sample C and images recorded.

2.3. X-ray topography
X-ray topographs were recorded using a Lang camera fitted to a rotating anode X-ray generator having a molybdenum target, zirconium filter and 0.2 mm x 0.2 mm apparent source size. The operating conditions of 40 kV, 40 mA produced a bright source of molybdenum Kα1 X-rays at 17.4 keV. A 250 µm slit collimator was used at a distance of 0.7 m from the source. Preliminary X-ray topographs were generated rapidly on dental film before high quality topographs, requiring longer exposure times, were recorded on nuclear plates (Ilford L4) and processed using standard techniques. Section topographs were recorded using a {533} reflection. With molybdenum Kα1 radiation, use of a {533} reflection allows samples to be set up in such a way that the plane sampled by the X-ray beam is within 2º of a {100} plane. It also allows topographs to be recorded with relatively little projection.
distortion because, at 81.37°, \(2\theta\) for the Bragg condition is fairly close to 90°. Exposure times were typically one hour.

3. Results and discussion

Figure 1 shows a \{533\} X-ray section topograph sampling a region close to the centre of sample A. The topograph indicates the dislocations are propagating very close to the [001] direction, which is parallel to the growth direction. The dislocation structure of sample A is typical of CVD diamond material grown upon a [001] orientated substrate, and demonstrates that growing on a substrate polished at a low off-axis angle does not significantly influence the dislocation propagation direction.

![Figure 1](image.png)

Figure 1. \{533\} X-ray section topograph sampling central region of sample A (substrate polished 4° from [001] about [010]).

Figure 2 shows a \{533\} X-ray section topograph sampling a region close to the centre of sample B. This sample has been grown on a [001] orientated substrate which has been polished 15° from [001] about [010]. Here we observe two distinct growth pseudo-sectors characterised by different dislocation propagation directions. There is an ‘on-axis’ growth pseudo-sector towards the left of the sample where the dislocations propagate in the [001] direction. To the right of the sample is an ‘off-axis’ growth pseudo-sector, where the dislocations propagate close to the [101] direction. From the analysis of this sample we suggest that the dislocation direction of propagation has been ‘switched’ from [001] to close to [101] via growth upon substrates with their major face polished off-[001], and the required off-axis angle is relatively small compared to the change in dislocation propagation direction. A 10° off-axis change has resulted in dislocations propagating 25° off the [001] direction. A growth pseudo-sector boundary is created between the ‘on-axis’ and ‘off-axis’ regions, which is likely to be defined by the difference in the relative growth rates for each pseudo-sector.

The surface morphology of sample B has been investigated using Nomarski microscopy and in particular the differences between the regions of ‘on-axis’ and ‘off-axis’ growth have been studied. The left hand image in figure 3 is a Nomarski micrograph of the surface of the ‘on-axis’ region of sample B showing regular, low angle steps that were flowing across the surface in a direction close to <100> when growth was terminated. In contrast, the right hand image in figure 3 is a Nomarski image of the surface of the ‘off-axis’ region of sample B showing coarse and irregular steps. Both images were recorded under the same magnification conditions. The surface morphology of sample B suggests the mode of growth is significantly different for the ‘on-axis’ and ‘off-axis’ regions, with the ‘off-axis’ growth having a higher proportion of riser growth.

![Figure 3](image.png)
Figure 2 \{533\} X-ray section topograph sampling central region of sample B (substrate polished 15° from [001] about [010]).

![Figure 2](image)

Figure 3 (a) Nomarski micrograph of the ‘on-axis’ growth surface of sample B. (b) Nomarski micrograph of the ‘off-axis’ growth surface of sample B. The width of the image in both cases is 144µm.

Figure 4 shows a \{533\} X-ray section topograph sampling a region close to the centre of sample C. This sample has been grown on a [001] orientated substrate which has been polished 10° from [001] about [010]. This sample exhibits ‘on-axis’ and ‘off-axis’ growth pseudo-sectors, with the dislocation line direction being [101] in the ‘off-axis’ region. This sample demonstrates the dislocation direction of propagation can be changed from [001] to [101] by growth on substrates polished off-axis by a relatively small angle.

Figure 5 shows a luminescence image of a polished \{001\} cross-section of sample C (the sample holder can be seen as a circular feature within image). The cross-section was produced to correlate closely with the region sampled by the \{533\} X-ray section topograph. The orange luminescence is due to nitrogen-vacancy defects and the diagonal striations are caused by variations of concentration due to the differential incorporation of such point defects in the regions of the crystal where growth has been on the terraces and risers of steps [2]. The degree of orange luminescence appears to differ between the ‘on-axis’ and ‘off-axis’ regions, with the ‘off-axis’ region appearing brighter. The difference in apparent brightness may be due to the ‘bright’ striations becoming brighter in the ‘off-
axis’ region or the ‘off-axis’ region possessing a higher proportion of ‘bright’ striations, suggesting differences in the proportion of terrace and riser growth in the two pseudo-sectors. Blue dislocation luminescence can also be observed to correlate with those dislocations imaged in the {533} X-ray section topograph in figure 4. Growth horizons running parallel to the substrate surface can also be observed shortly after the start of growth and then in the early stages of growth.

Figure 4 {533} X-ray section topograph sampling central region of sample C (substrate polished 10º from [001] about [010]).

Figure 5 UV-excited photoluminescence image of a cross-sectional slice of sample C.

The surface morphology and diagonal striations seen in the DiamondView image confirm step-flow growth [10]. Martineau et al. [10] proposed a model for the step flow growth and dislocation interaction in which the dislocation direction of propagation was parallel to the growth direction within terrace growth ([001] line direction) and at 45º to the growth direction ([101] line direction) within riser growth. The risers in the study were inclined only by approximately 20º (the dislocations
did not propagate perpendicular to the riser surfaces). It could be seen in TEM images that the 

dislocations propagated in the [101] direction during riser growth. Geometric arguments coupled with theoretcal values for dislocation core energies per unit length [6 – 8], led to the suggestion that the energy of the [101] dislocation is less than that of a dislocation with a line direction perpendicular to the riser surface, and if a riser were incumbent on the dislocation it would change direction from [001] to [101]. A critical riser angle was proposed and calculated using dislocation core energies per unit length from \textit{ab initio} calculations [6 - 8], above which [001] dislocations switch to [101] dislocations.

In the present study we have observed the switching of dislocation line direction from [001] to close to [101], or [101] in some cases, but the relatively low spatial resolution achievable with X-ray topography has made it difficult to determine whether the dislocations are straight or made up of segments with different directions. Figure 6(a) illustrates two mechanisms by which the angle of the growth horizon with respect to [001] and terrace/riser growth may cause dislocations to propagate in the [101] direction. In (a), due to the fact that the growth horizon is parallel to the off-axis substrate both terraces and risers are inclined at an angle above the critical angle needed to switch dislocation line direction from [001] to [101]. In figure 5 the growth horizons in the ‘off-axis’ region appear to be parallel to the substrate, which is consistent with the terraces being inclined at an angle possibly greater than that required to convert [001] dislocations to [101]. Figure 6(b) illustrates how terrace and riser growth could cause dislocations to propagate at a direction close to [101]. The surface morphology of sample B shows obvious differences in the step flow growth for the ‘on-axis’ and ‘off-axis’ pseudo-sectors. The ‘on-axis’ region shows regular low angle steps, and terrace growth dominates over riser growth. In contrast, the ‘off-axis’ region shows very coarse irregular steps, where neither terrace or riser growth dominates. The increase in riser content for the ‘off-axis’ region will lead to a deflection of the dislocations toward the [101] direction, because during riser growth the dislocation line direction will be switched to [101]. For this case, an average dislocation line direction of 25º away from [001] is not inconsistent with an approximately equal riser and terrace content with the riser growth resulting in [101] propagation and the terrace growth results in [001] propagation.

![Figure 6](image-url) **Figure 6** Schematic cross-sectional view of the effect of step flow growth on dislocations during growth on off-axis substrates. Bold lines represent dislocations, dashed lines boundaries between terrace and riser growth and dotted lines growth horizons. (a) Both terrace and riser angles are above critical value to switch dislocation line direction to [101]. (b) Riser angles are above critical value to switch dislocation line direction to [101].
4. Conclusion
Single crystal CVD diamond samples grown on (001) substrates polished off-axis by between 10° and 15° from (001) have been studied using X-ray topography, Nomarski microscopy and luminescence imaging. Results clearly show dislocations propagating in, or close to, the [101] direction in some regions of the sample rather than the [001] direction which is more usual for CVD diamond samples grown on (001) substrates polished on-axis. The off-axis angle required to deflect the dislocations is relatively small compared to the resulting angle of deflection of the dislocations (25° - 45°). The model relating the dislocation line direction with surface inclination as a result of step-flow growth as proposed by Martineau et al. [10] has been used to explain the deflection of dislocations during growth on off-axis substrates.

Two mechanisms are proposed for the deflection of dislocations during growth on off-axis substrates. It is possible that either the orientation of the growth horizon with respect to (001) or differences in the riser and terrace content between on-axis and off-axis growth pseudo-sectors, or a combination of the two, play a role in diverting dislocations from [001] to [101] or close to [101]. Our work here suggests that either model may dominate in different scenarios.

Further work, such as TEM studies, to investigate the case where the dislocations propagate close to the [101] direction would provide a better understanding of the above mechanisms. The high resolution provided by TEM could enable determination of the extent to which dislocations are straight or made up of alternating segments. Also, stopping the growth run before the ‘on-axis’ growth dominates would allow the surface morphology of the ‘off-axis’ region to be studied in greater detail and the relative proportions of terrace and riser growth to be accurately determined.

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