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Direct observations of crystal defects in polycrystalline diamond

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ABSTRACT

Crystal defects are abundant in synthetic diamond produced by chemical vapor deposition (CVD). We present the first images of crystal defects in a bulk polycrystalline CVD diamond sample using general electron channeling contrast imaging (ECCI) in a field emission scanning electron microscope (FE-SEM). For enhancement of channeling contrast of this material, we introduce a novel protocol for diamond surface preparation that involves acid etching. Using this protocol, we imaged three types of crystal defects including twins, stacking faults and dislocations. Each defect was identified based on its appearance in electron channeling contrast (ECC) micrographs. We analyzed grains containing twins and dislocations using electron backscatter diffraction (EBSD) crystal orientation mapping. We found a large population of grains that contained Σ3 type twins on {111} planes with a 60°⟨111⟩ angle–axis pair of misorientation for twin boundaries. In addition, we identified {111} stacking faults and {111} *helical* dislocations. These observations are in agreement with reports of crystal defects in CVD diamond thin foils studied by a transmission electron microscope (TEM).

1. Introduction

Diamond is a unique material due to a combination of remarkable physical, chemical and mechanical properties. It has the highest hardness and thermal conductivity of any material, high electrical and wear resistivity as well as excellent thermal and chemical stability. These characteristics make diamond a suitable material for important technical and scientific applications in a variety of industries including aerospace and defense, power electronics, lasers and optics as well as in materials research [1].

Diamond exists in natural and synthetic forms. Synthetic diamond is commonly produced using chemical vapor deposition (CVD). The nucleation and growth process of CVD diamond is associated with the formation of crystal defects including twins, stacking faults and dislocations [2]. Characterization of these defects is critical in establishing the relationships between the CVD process parameters and resulting diamond microstructures in order to produce CVD diamond with desired properties [3].

Characterization of crystal defects in diamond has been previously performed using a transmission electron microscope (TEM) [4–8]. Diamond thin foil preparation is a challenging task since conventional mechanical grinding and polishing techniques are not applicable due to diamond's extreme hardness. Instead, thin foils are prepared by ion milling [7,9], cleavage [4], laser cutting [5] and focused ion beam (FIB) [10]. Owing to the harsh conditions used to thin the diamond, all of these techniques inevitably introduce additional defects into the foil making it difficult to distinguish them from those that are present in the bulk sample.

Electron channeling contrast imaging (ECCI) in a field emission scanning electron microscope (FE-SEM) with a nanoscale spatial resolution is an alternative tool for characterization of crystal defects in a bulk sample. Electron channeling contrast (ECC) is based on modulation of the backscattered electron (BSE) signal as a function of local variations in the crystal orientation near crystal defects [11–13]. Comprehensive reviews of the theory [14–17], practice, and application [18–21] of ECCI can be found in [22,23]. There are no previous studies that use ECCI for microstructure characterization of bulk diamond. Our literature survey shows only a few accounts of imaging crystal defects in diamond using charge-induced secondary electron (SE) imaging in a SEM [24–26]. All other characterization work on diamond is limited to imaging surface morphology using standard SE imaging in a SEM. Examples can be found in [27–31]. The absence of ECCI on crystal defects in diamond is not surprising due to the challenges associated with obtaining a flat surface at the nanoscale as well as obtaining sufficient BSE signal from a low atomic number material like diamond. This study introduces a novel protocol for sample preparation and microscope operation conditions to overcome these difficulties.

In this paper, we report the first direct observations of twins, stacking faults and dislocations in a bulk polycrystalline CVD diamond sample using ECCI in a FE-SEM. We introduce surface etching for

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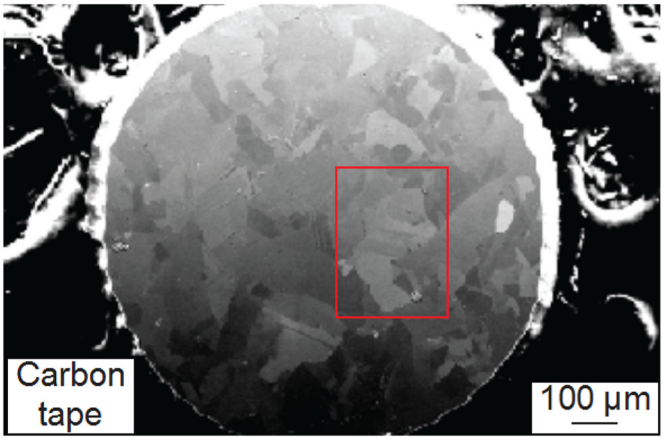

Fig. 1. Electron channeling contrast (ECC) micrograph of the bulk polycrystalline CVD diamond surface in a field emission scanning electron microscope (FE-SEM). Grains with different crystal orientation exhibit channeling contrast. Grain size ranged from ~60 µm to ~130 µm.

enhancement of channeling contrast of diamond. Furthermore, we use electron backscatter diffraction (EBSD) crystal orientation mapping to analyze grains containing crystal defects. Our results show the unprecedented potential of ECCI in FE-SEM for imaging crystal defects in diamond as an alternative technique to diamond thin foil examination in TEM.

2. Experimental

The material used for this study is a polycrystalline CVD diamond rod produced by Applied Diamond Inc. (http://usaplieddiamond.com). The sample is a rod of 1 mm diameter and 500 µm thickness with optically transparent and polished faces.

2.1. Surface Preparation

The sample was immersed in a room-temperature hydrochloric-nitric acid solution (12 ml HCl + 8 ml HNO_3 + 100 ml C_2H_6O) for 30 min. The sample was ultrasonically cleaned in denatured ethanol for 30 min immediately after etching. The sample was then rinsed with denatured ethanol and dried in air. No surface coating was applied to the sample prior to insertion into the microscope. We repeated the etching and cleaning steps after every 5 h of ECCI and EBSD to remove the surface contamination.

2.2. Microscope Operation Conditions

We used a ZEISS SIGMA VP FE-SEM to perform ECCI and a JEOL JSM-6700F FE-SEM to perform EBSD on our sample. For ECCI, we first placed the sample face down on a standard conducting carbon tape on an aluminum stub. The sample was then flipped over and imaged. The reason for this step is to deliberately contaminate the surface with a small amount of carbon. The carbon remaining on the surface provides sufficient surface conductivity without applying a continuous carbon coat which would diminish the channeling contrast. ECCI was performed using a four-quadrant silicon photodiode BSE detector inserted below the pole piece at a 30 keV beam energy, a 7–8 mm working distance, a 120 µm objective aperture and in high current mode. A slow scan speed with an image acquisition time of 5.6 min was used for each micrograph to achieve a high BSE signal to noise ratio. The microscope was operated in high vacuum mode. ECCI was performed at low stage tilt positions (± 5°) for contrast reversal of crystal defects. We investigated the conditions for channeling contrast reversal to confirm the presence of dislocations and stacking faults in our images and distinguish them from the topographical artifacts in the grains due to acid-etching of surface. In the discussion of all ECC micrographs presented in this study, a bright contrast refers to a high BSE intensity and a dark contrast refers to a low BSE intensity. Note that we did not control the channeling conditions to perform ECCI.

EBSD crystal orientation mapping was performed using a 70° pre-tilt holder with a Nordlys Oxford system at a 20 keV beam energy, a 21–22 mm working distance and in high current mode. The EBSD crystal orientation maps were acquired at a 0.4–2 µm step size using the *HKL Channel5 Flamenco* software (Oxford Instruments, Abingdon, Oxfordshire, UK). For background correction, we used static and dynamic calibrations, a total of 200 frames and a divide operation. We selected a dynamic stretch for contrast enhancement and three frames for noise reduction of EBSD patterns. We used a 4 × 4 binning and a low gain function for the camera. We constructed pole figures using the *HKL Channel5 Mambo* post-processing software. In our reconstructed pole figures, the cluster of raw orientation data is replaced by a circle for better visualization of crystallographic relationships.

All measurements on ECCI micrographs were carried out using the

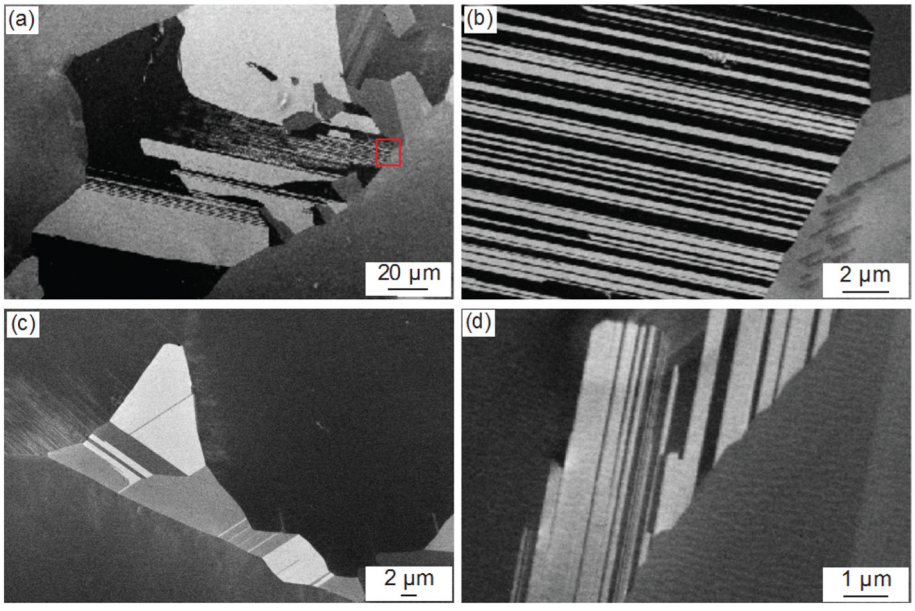

Fig. 2. Example of twinning in a polycrystalline CVD diamond sample. (a) Low magnification electron channeling contrast (ECC) micrograph of a twinned grain and (b) a higher magnification ECC micrograph of the twinned region in (a) indicated by the red square. Twins are in the form of parallel and straight bands with a sharp channeling contrast that run across the width of host grain. Wiggles at the twin boundaries in (b) are artifact due to astigmatism in the image. (c) and (d) are more examples of ECC micrographs of twins in diamond. The ripples in (d) are due to surface acid etching. The zone of interest corresponding to (a) is indicated with a red square in Fig. 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)