Diamond & Related Materials 18 (2009) 713–717

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Crystallographic anisotropy of growth and etch rates of CVD diamond

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ARTICLE INFO

Available online 13 December 2008

Keywords:
Diamond CVD
Homoepitaxy
Etching
Orientation

ABSTRACT

The investigation of orientation dependent crystal growth and etch processes can provide deep insights into the underlying mechanisms and thus helps to validate theoretical models. Here, we report on homoepitaxial diamond growth and oxygen etch experiments on polished, polycrystalline CVD diamond wafers by use of electron backscatter diffraction (EBSD) and white-light interferometry (WLI). Atomic force microscopy (AFM) was applied to provide additional atomic scale surface morphology information. The main advantage of using polycrystalline diamond substrates with almost random grain orientation is that it allows determining the orientation dependent growth (etch) rate for different orientations within one experiment. Specifically, we studied the effect of methane concentration on the diamond growth rate, using a microwave plasma CVD process. At 1% methane concentration a maximum of the growth rate near <100> and a minimum near <111> is detected. Increasing the methane concentration up to 5% shifts the maximum towards <110> while the minimum stays at <111>. Etch rate measurements in a microwave powered oxygen plasma reveal a pronounced maximum at <111>. We also made a first attempt to interpret our experimental data in terms of local micro-faceting of high-indexed planes.

1. Introduction

Over the past 20 years, progress in the field of microwave plasma enhanced CVD (MPCVD) has led to the synthesis of high quality diamond [1–2], which forms the basis for a variety of applications [3]. Much effort has been devoted to the optimization of the growth of single diamond crystals [4–6] by controlling deposition parameters such as temperature, gas composition, and substrate orientation. The underlying growth processes have been studied by performing growth experiments on surfaces which are slightly misoriented from low index planes [7–11]. However, a unifying atomic scale growth model explaining the observed growth kinetics on different diamond surface orientations is still missing. The purpose of the present work is to generate the experimental data necessary to develop a deeper understanding of the surface processes during diamond CVD.

A common crystallographic approach to obtain information about displacement velocities and growth morphologies of high-index crystal planes are sphere growth experiments. The idea is that an ideal crystal sphere exhibits all crystallographic faces equally and therefore supplies detailed information about the growth mechanisms. A successful diamond sphere growth experiment under CVD conditions published by van Enckevort et al. [12] showed that the surface processes of diamond growth depends strongly on substrate orientation. However, the preparation, characterization and handling of diamond spheres for growth rate experiments is challenging and makes systematic studies difficult.

Here, we describe the results of homoepitaxial growth and oxygen etch experiments on polished polycrystalline CVD diamond wafers. Our samples exhibit weak textures and therefore all crystallographic orientations are present at the surface similar to the situation in a sphere growth experiment, and thus allow us to obtain the complete orientational growth (etch) rate dependence within one experiment.

2. Experimental

Large-grained polycrystalline diamond samples with an average thickness of 250 µm were grown on <001> Si substrates, 25 mm in diameter and 5 mm in thickness, using an ellipsoidal microwave plasma reactor operated at 2.45 GHz microwave frequency [13]. Deposition was performed under the following conditions: 6 kW microwave output power, 150 mbar gas pressure, 300 sccm flow rate and 1% CH_4 in H_2. The as-grown polycrystalline diamond surfaces were polished to a mirror-like surface finish with roughness values around 5 nm (rms).

All samples exhibited little pronounced fibre textures, measured by EBSD, which vary from sample to sample. Typically the maximum of the orientational distribution is near <101> or on the <101>–<001> line, respectively. An example of the orientational distribution of surface grains is shown in Fig. 2b. In contrast to former works of Wild et al. [14] on highly textured polycrystalline diamond films the detected weak textures could not be explained by the Van der Drift mechanism.

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doi:10.1016/j.diamond.2008.11.034

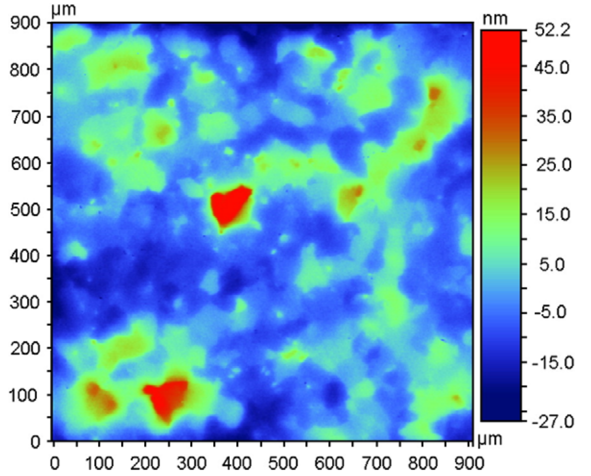

Fig. 1. Topography of a specimen obtained by whitelight interferometry after polishing. High grains, i.e. grains with a high abrasion resistance, are coloured red, low grains blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Possible reasons therefore are twinning, which also shows up in the EBSD data (Fig. 2a), and deviation from former growth parameters, due to the ellipsoidal cavity reactor used for the present study. To facilitate the analysis of our growth experiments, we machined a grid of reference lines (1×1 mm^2 cell size) into the diamond surface using a Nd:YAG laser. Finally, the samples were carefully cleaned in acetone, isopropanol, rinsed with methanol and dried under a stream of dry nitrogen gas.

Using these samples as substrates, we then studied the effect of crystallographic surface orientation on both growth and etch rates of diamond using the following experimental procedure: First, we measured the surface topography and generated a grain orientation map of one of the 1×1 mm^2 cells using a combination of whitelight interferometry and electron backscatter diffraction (EBSD). This data set provides the baseline for the analysis of the following growth/etch experiments. Next, we deposited (or etched) a few hundred nm of diamond on (or from) the sample (5–15 min plasma exposure), and measured the surface topography of the same surface area again. To obtain the average growth/etch rate the surface of the sample was partially masked by a thin sheet of polycrystalline diamond. Additional atomic scale information was obtained by atomic force microscopy (AFM). In order to correlate the grain orientation map (EBSD data) with the topographic (height) information obtained by whitelight interferometry we developed a computer program which automatically compensates for image distortions between the two data sets by using prominent surface features as landmarks. We then corrected the data for prior height differences between the surface grains caused by the anisotropic polishing behaviour of polycrystalline diamond. Finally, the grain orientation–growth (etch) rate correlation was visualized by plotting the data into a stereographic projection triangle in the form of circles. Here, the position of the circles indicates the grain orientation, their colour the grain height (relative growth rate) and their diameter the grain size. Specifically, we studied the effect of methane concentration (1–5% methane in hydrogen) of the growth kinetics using the following conditions: 300 sccm total flow rate, 150 mbar gas pressure, 6 kW microwave power, and substrate temperatures of 750–790 °C (measured by an optical pyrometer). Etching experiments with 2% oxygen in hydrogen were performed in the same reactor under similar conditions.

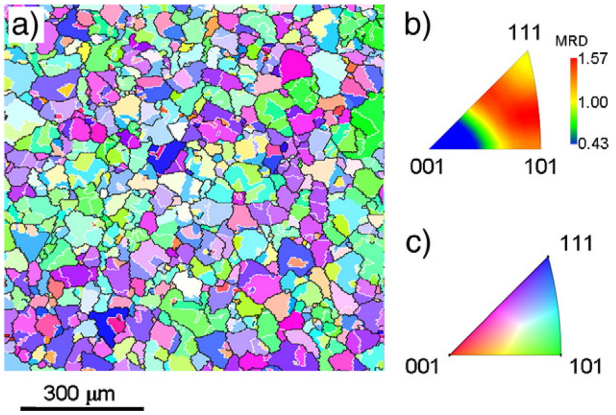

Fig. 2. a) EBSD map of the same surface area as in Fig. 1; black lines indicate normal grain boundaries, white lines twin boundaries b) IPF plot showing the orientation distribution as a function of multiples of random distribution (MRD). c) Correlation between colour and orientation for picture a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

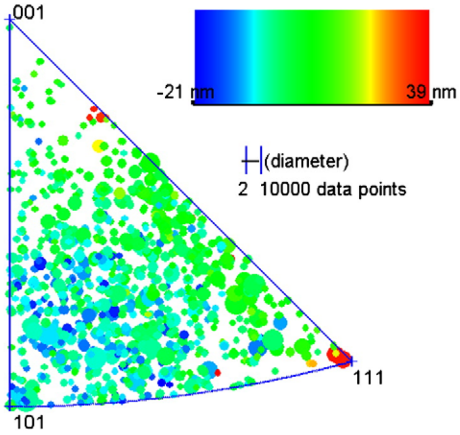

Fig. 3. A typical orientation height correlation after polishing. The position of the circles in the stereographic triangle corresponds to the crystallographic orientation of the grains, the colour to their relative height. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. Anisotropic abrasion resistance

In order to be able to analyze the growth (etch) experiments discussed in the following sections it is necessary to characterize the surface topography of our polished polycrystalline diamond substrates. A typical example of the surface topology is shown in Fig. 1. Already a simple visual comparison of this image with the corresponding EBSD grain orientation map shown in Fig. 2 reveals that grains with orientations near <111> stick out of the surface and therefore must have a higher abrasion resistance. Fig. 3 shows the

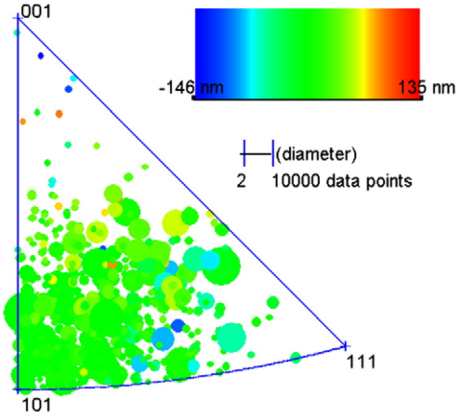

Fig. 4. Orientation height correlation after 5 min oxygen plasma treatment.