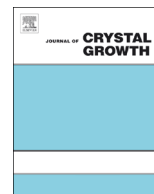




ELSEVIER

Contents lists available at ScienceDirect

## Journal of Crystal Growth

journal homepage: [www.elsevier.com/locate/jcrysgr](http://www.elsevier.com/locate/jcrysgr)

# Effect of methane concentration in hydrogen plasma on hydrogen impurity incorporation in thick large-grained polycrystalline diamond films

C.J. Tang<sup>a,b,\*</sup>, A.J.S. Fernandes<sup>b</sup>, X.F. Jiang<sup>a</sup>, J.L. Pinto<sup>b</sup>, H. Ye<sup>c</sup><sup>a</sup> Department of Physics, Jiangsu Key Laboratory for Advanced Functional Materials, Changshu Institute of Technology, Changshu 215500, PR China<sup>b</sup> Department of Physics, I3N (Institute for Nanostructures, Nanomodelling and Nanofabrication), University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal<sup>c</sup> School of Engineering and Applied Science, Aston University, Aston Triangle, Birmingham, B4 7ET, UK

## ARTICLE INFO

## Article history:

Received 13 May 2015

Received in revised form

16 June 2015

Accepted 17 June 2015

Communicated by: P. Rudolph

Available online 26 June 2015

## Keywords:

A1. Characterization

A1. Defects

A3. Microwave plasma assisted chemical vapor deposition process

B1. Diamond

## ABSTRACT

We investigate the impact of methane concentration in hydrogen plasma on the growth of large-grained polycrystalline diamond (PCD) films and its hydrogen impurity incorporation. The diamond samples were produced using high CH<sub>4</sub> concentration in H<sub>2</sub> plasma and high power up to 4350 W and high pressure (either 105 or 110 Torr) in a microwave plasma chemical vapor deposition (MPCVD) system. The thickness of the free-standing diamond films varies from 165 μm to 430 μm. Scanning electron microscopy (SEM), micro-Raman spectroscopy and Fourier-transform infrared (FTIR) spectroscopy were used to characterize the morphology, crystalline and optical quality of the diamond samples, and bonded hydrogen impurity in the diamond films, respectively. Under the conditions employed here, when methane concentration in the gas phase increases from 3.75% to 7.5%, the growth rate of the PCD films rises from around 3.0 μm/h up to 8.5 μm/h, and the optical active bonded hydrogen impurity content also increases more than one times, especially the two CVD diamond specific H related infrared absorption peaks at 2818 and 2828 cm<sup>-1</sup> rise strongly; while the crystalline and optical quality of the MCD films decreases significantly, namely structural defects and non-diamond carbon phase content also increases a lot with increasing of methane concentration. Based on the results, the relationship between methane concentration and diamond growth rate and hydrogen impurity incorporation including the form of bonded infrared active hydrogen impurity in CVD diamonds was analyzed and discussed. The effect of substrate temperature on diamond growth was also briefly discussed. The experimental findings indicate that bonded hydrogen impurity in CVD diamond films mainly comes from methane rather than hydrogen in the gas source, and thus can provide experimental evidence for the theoretical study of the standard methyl species dominated growth mechanism of CVD diamonds grown with methane/hydrogen mixtures.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Diamond material has been research topic for many years due to its many excellent physical and chemical properties. Among diamond research, hydrogen impurity in diamond is one of the important subjects that have attracted many researchers from the world for a long time. Usually, according to the source or synthetic method, diamond can be divided into three major types, such as natural diamond single crystal, high-pressure high-temperature

(HPHT) synthetic diamond single crystal and chemical vapor deposited (CVD) diamonds (usually as polycrystalline films). Therefore, hydrogen defects in natural diamond single crystals [1–3] were first studied in more details ever since 1980s. Recently, investigation of hydrogen defects in HPHT synthetic diamond single crystal with intentional hydrogen doping has revealed interests [4,5]. Generally CVD diamond films are grown in hydrogen rich atmosphere with a few percentage of methane as carbon source, and thus hydrogen has been found as an impurity incorporated unavoidably into the growing CVD diamond films during the growth process [6–8]. It is widely accepted that the main growth species in standard diamond CVD is the CH<sub>3</sub> radical, which adds to radical sites (dangling bonds) create on the diamond surface following hydrogen abstraction by H atoms [9,10], so called the standard growth mechanism of CVD diamonds.

\* Corresponding author at: Department of Physics, I3N (Institute for Nanostructures, Nanomodelling and Nanofabrication), University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal. Tel.: +351 234 370356; fax: +351 234 378197.

E-mail address: [tang.chunjiu@ua.pt](mailto:tang.chunjiu@ua.pt) (C.J. Tang).

It is well-known that CVD diamond product is the overall thermodynamic effects of all growth parameters, such as microwave power, pressure, substrate temperature, and methane concentration in hydrogen in case of only methane/hydrogen gas mixtures are employed in microwave plasma assisted CVD (MPCVD) systems [11]. Although CVD diamond has been developed for more than three decades and the growth parameter window of large-grained polycrystalline diamond films have been well established in general [10,11], so far it is not yet fully explored all the possible range of each of the growth parameters for CVD diamond growth, not even clearly understood the growth mechanism, defect formation and impurity incorporation such as hydrogen incorporation in CVD diamond films.

To obtain a diamond film with desired morphology and quality combined with controlled mechanical, electrical and electronic properties requires a detailed understanding of the many parameters affecting growth. There are some reports in the literature about the effect of methane concentration on diamond growth by different CVD techniques such as MPCVD [12] and hot-filament CVD [13,14]. Recently, it has been reported that control over the grain size ranging from several  $\mu\text{m}$  (namely microcrystalline diamond (MCD)) to a few nm (i.e. nanocrystalline diamond (NCD)) was achieved by adjusting the  $\text{CH}_4$  content (ranging from 2% to 5%) of the  $\text{CH}_4/\text{H}_2$  feed gas using microwave power 3000 W, and pressure 35–45 mbar on Si substrates [15]. Although the authors did show the CH stretching band in the FTIR spectra of the diamond films as a function of methane concentration in the supporting information [15], they did not study the impact of methane concentration on hydrogen impurity incorporation in CVD diamond films. Since there is no report in the literature on the impact of methane concentration on hydrogen impurity incorporation in CVD diamond films, in the present study, we investigate for the first time the role of methane concentration in hydrogen plasma on diamond growth and hydrogen impurity incorporation in diamond films by exploring high methane concentration, high pressure and high power in a 5 kW MPCVD reactor. It is worth to note that the specific role of each growth parameter on CVD diamond growth under different conditions or by different growth techniques also strongly depends on all the other growth parameters. In other words, it is worth to bear in mind that even the methane content is the same, the effect of methane concentration on diamond growth and hydrogen impurity incorporation under high pressure and high power conditions is different from that under low pressure and low power conditions. The present study can provide experimental evidence for the so called standard growth mechanism of CVD diamond using conventional methane/hydrogen plasma [9] and shed light into the defect formation and hydrogen impurity incorporation mechanism in CVD diamonds.

## 2. Experimental details

The four diamond samples investigated here were produced using a 5 kW ASTeX PDS-18 MPCVD reactor and named as A to D. Samples A and C were grown on small (100) silicon slice of  $2.5 \times 2.5 \text{ cm}^2$  area and 1 mm thick, while samples B and D were grown on (100) silicon wafers of 5.08 cm in diameter and 3 mm thick. Film A was grown directly on mirror-like Si substrate without any pre-treatment, while the other three silicon substrates were pre-treated with diamond powder (0.5  $\mu\text{m}$ ). As mentioned in details in our previous publication [16], in such high power MPCVD reactor, substrate surface temperature is mainly controlled by the input microwave power, and can be slightly adjusted by the thickness of the silicon substrate used for diamond growth and the use of different type of Mo holders, whose

temperature was monitored by a thermocouple embedded into the water cooled holder stage. There are two type of Mo holder, namely so called “cold” and “hot” holder, their only difference is on the bottom contact area with the graphite supporting system. More contact area results in better cooling effect on the Mo holder, therefore lower temperature can be obtained when the input power is kept constant, hence “cold” type Mo holder is named, on the contrary, the less contact area holder is called “hot” type holder. For the diamond film growth, “cold” type Mo holder were used for two samples A, C, and “hot” type one for the other two samples B, D. Pressure was 105 Torr (135 mbar) for sample A and 110 Torr (142 mbar) for the rest samples. The Mo holder temperature was 347 °C for sample A, and 301 °C for sample B, 320 °C for sample C and 311 °C for sample D during the diamond deposition process. The other growth parameters of the samples are listed in Table 1 together with some characteristics of the diamond films for comparison.

The morphologies of the diamond films were characterized by using a Hitachi S-4100 scanning electron microscope (SEM) operated at 25 kV. The crystalline phase and orientation or texture of the samples was studied by X-ray diffraction (XRD). Micro-Raman spectra of the samples were taken using Jobin Yvon (Horiba) Labram HR800 with HeCd laser of 325 nm to check their diamond crystalline quality. The central thickness of the sample was measured by using the cross-sectional SEM micrograph and the edge of the sample was measured by using micrometer or optical microscope. The middle infrared transmittance spectra with 4  $\text{cm}^{-1}$  resolution were obtained at normal incidence in an evacuated chamber of an IFS 66V FTIR spectrometer manufactured by Bruker Optics. A KBr beam-splitter and a DTGS detector with KBr window were used to cover the frequency range 400–4000  $\text{cm}^{-1}$ .

## 3. Results and discussion

Just viewed by our naked eyes, free-standing films A is light gray and film B is gray in color, while films C and D are black in color, showing the worse quality of the latter two films grown with higher methane concentration. Fig. 1 shows the SEM micrographs of different magnifications taken from the growth surfaces of the four films for comparison. Large-grained polycrystalline nature of all the films can be clearly seen from the large-scale SEM images shown in the left column of Fig. 1. Further higher magnified SEM images (right column of Fig. 1) clearly demonstrate the different degree of facet roughness or crystallinity of a crystallite of the films. In other words, from film A to D, the crystallite facets look ranging from atomic smooth to surface roughing due to increasing defect density, demonstrating degradation of their crystallinity.

In order to further demonstrate the structural defects of film D in more detail, Fig. 2a shows a high resolution SEM image taken from a crystallite facet as marked by square shown in Fig. 1h. For

**Table 1**

Growth parameters such as microwave power,  $\text{CH}_4/\text{H}_2$  flow (unit SCCM), type of Mo holder, and some characteristics of the samples, namely thickness, FWHM of the diamond Raman peak at around 1332  $\text{cm}^{-1}$ , growth rate and infrared active bonded hydrogen impurity content (calculated from the integrated area of the CH stretching band divided by the film thickness).

Sample	Power (kW)	$\text{CH}_4/\text{H}_2$ (SCCM)	Mo holder	Thickness ( $\mu\text{m}$ )	FWHM ( $\text{cm}^{-1}$ )	Growth rate ( $\mu\text{m}/\text{h}$ )	Bonded H content
A	4.00	16/400	Cold	270	5.0	3.3	141
B	4.00	15/400	Hot	165	9.1	3.0	424
C	4.35	30/400	Cold	430	11.1	7.2	320
D	4.35	30/400	Hot	430	11.4	8.5	896

Download English Version:

<https://daneshyari.com/en/article/1789892>

Download Persian Version:

<https://daneshyari.com/article/1789892>

[Daneshyari.com](https://daneshyari.com)