



High rate growth of nanocrystalline diamond films using high microwave power and pure nitrogen/methane/hydrogen plasma



C.J. Tang^{a, b, *}, A.J.S. Fernandes^a, Marco Granada^a, J.P. Leitão^a, S. Pereira^c, X.F. Jiang^b, J.L. Pinto^a, H. Ye^d

^a Department of Physics, I3N, University of Aveiro, 3810-193 Aveiro, Portugal

^b Department of Physics, Jiangsu Key Laboratory for Advanced Functional Materials, Changshu Institute of Technology, Changshu 215500, PR China

^c Department of Physics, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

^d School of Engineering and Applied Science, Aston University, Aston Triangle, Birmingham B4 7ET, UK

ARTICLE INFO

Article history:

Received 2 November 2014

Received in revised form

19 March 2015

Accepted 20 March 2015

Available online 28 March 2015

Keywords:

Nanocrystalline diamond films

High growth rate

Nitrogen/methane/hydrogen plasma

Nitrogen induced growth rate enhancement

High power MPCVD

ABSTRACT

In this work, we investigate the impact of minute amounts of pure nitrogen addition into conventional methane/hydrogen mixtures on the growth characteristics of nanocrystalline diamond (NCD) films by microwave plasma assisted chemical vapour deposition (MPCVD), under high power conditions. The NCD films were produced from a gas mixture of 4% CH₄/H₂ with two different concentrations of N₂ additive and microwave power ranging from 3.0 kW to 4.0 kW, while keeping all the other operating parameters constant. The morphology, grain size, microstructure and texture of the resulting NCD films were characterized by using scanning electron microscope (SEM), micro-Raman spectroscopy and X-ray diffraction (XRD) techniques. N₂ addition was found to be the main parameter responsible for the formation and for the key change in the growth characteristics of NCD films under the employed conditions. Growth rates ranging from 5.4 μm/h up to 9.6 μm/h were achieved for the NCD films, much higher than those usually reported in the literature. The enhancing factor of nitrogen addition on NCD growth rate was obtained by comparing with the growth rate of large-grained microcrystalline diamond films grown without nitrogen and discussed by comparing with that of single crystal diamond through theoretical work in the literature. This achievement on NCD growth rate makes the technology interesting for industrial applications where fast coating of large substrates is highly desirable.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Nanocrystalline diamond (NCD) films not only possess most of the excellent properties of diamond, but also have increased smoothness (low surface roughness) due to their small grain size, ranging from several hundreds of nanometres to the nano scale (below 100 nm) [1,2]. Therefore, NCD films have received great attention in recent years as a potential nanomaterial for many new applications in bio medicine [3], quantum information (NV) centres [4] and optoelectronic devices [5]. NCD films have been produced using Ar/CH₄ feeding gases [6] or through the introduction of nitrogen additive into CH₄/H₂ gas mixtures [5,7–9]. For example, it was recently reported that a high growth rate 2.4 μm/h was

achieved for ultrananocrystalline diamond films grown by bias enhanced nucleation and growth process using CH₄/Ar plasma [10]. It has been shown that the amount of nitrogen added into the gas phase has significant influence on the electrical properties of the produced nitrogen incorporated NCD films [11]. Furthermore, it has been demonstrated that N-doped NCD films fabricated by CH₄/H₂/N₂ plasmas without Ar are favourable for achieving high-performance diamond-based optoelectronic devices [5]. Inspired by this study, the present work focuses on fast fabrication and characterization of N-doped NCD films using only CH₄/H₂/N₂ plasma in order to achieve optimum nanomaterials for high-performance diamond-based optoelectronic devices.

NCD films have been deposited through large amounts of nitrogen addition into conventional methane-hydrogen plasma using microwave power below 1500 W [7,8,11], the growth rate being reduced from 1 μm/h to 0.1 μm/h when the grain size decreased from 200 nm to 5 nm [8]. So far, the growth rate of most NCD films reported in the literature is in the order of magnitude from 0.1 μm/h

* Corresponding author. Department of Physics, I3N, University of Aveiro, 3810-193 Aveiro, Portugal. Tel.: +351 234 370356; fax: +351 234 378197.

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

to 1 $\mu\text{m}/\text{h}$. It is worth to emphasize the fact that low growth rate is still one of the main hurdles that hinder the realistic applications for chemical vapour deposited (CVD) diamonds [12]. Increasing the growth rate of CVD diamond films can reduce the product costs. Therefore, this urges the intensive researches on nitrogen doping effect on enhancing diamond growth rate both experimentally [13] and theoretically [14].

Nowadays, MPCVD has become dominant in both industrial and research facilities worldwide [15,16]. It is known that in comparison with HFCVD and low power (<3 kW) MPCVD, high power (≥ 3 kW) MPCVD processes are efficient for producing high quality large-grained microcrystalline diamond (MCD) films at high growth rate usually around 3 $\mu\text{m}/\text{h}$ [16–19]. Previously we have obtained NCD films at high growth rate 4.6 $\mu\text{m}/\text{h}$ using high microwave power 4.0 kW through air addition namely simultaneous nitrogen and oxygen addition [20]. However, so far there has been no attempt on growing NCD films using pure N_2 addition into CH_4/H_2 plasma at powers exceeding 3 kW and very few knowledge is available on the influences of the growth parameters on the growth mechanisms and characteristics of NCD or N-doped NCD films. Therefore, in the present work, the fabrication of NCD films is reported attaining very high growth rates up to 9.6 $\mu\text{m}/\text{h}$ by using $\text{N}_2/\text{CH}_4/\text{H}_2$ gas mixtures in high power mode (3.0 kW; to 4.0 kW) in a 5 kW MPCVD system. Furthermore, the relationship between the growth conditions, the growth characteristics and growth rate of the NCD films is investigated. The factors responsible for the formation of NCD and its growth rate enhancement under high power conditions are briefly discussed and compared with our previous work and other results from the literature.

2. Experimental details

The diamond films were produced in a 5 kW ASTeX PDS-18 MPCVD reactor. Square silicon pieces of $25 \times 25 \times 1 \text{ mm}^3$, are used as substrates and pre-scratched with diamond powder (0–0.5 μm) to enhance diamond nucleation. For each deposition, a pre-treated Si substrate was directly placed on the centre of a Mo holder (5.08 cm in diameter), whose temperature was monitored by a thermocouple embedded into the water cooled holder stage. The main growth parameters such as pressure (135 mbar), H_2 flow (400 sccm), and CH_4 flow (16 sccm, corresponding to 4 Vol% CH_4 in H_2), were kept constant for all the deposited NCD films. It is remarked that this set of parameters has been commonly used for the growth of high quality large-grained microcrystalline diamond (MCD) in the early works using the same reactor. The microwave power was varied from 3.0 kW to 4.0 kW and the N_2 flow was selected to be either 1 sccm or 1.6 sccm, corresponding to N/C ratios of 0.125 or 0.2, respectively. The thermocouple readings during diamond deposition were 308 $^\circ\text{C}$ for ND1, 349 $^\circ\text{C}$ for ND2, and 372 $^\circ\text{C}$ for ND3, respectively. The deposition time was 5.25 h for sample ND1, 5.58 h for ND2 and 4.67 h for ND3. The thickness of the produced films was measured by optical microscopy using a micrometre ruler. Table 1 lists, for each sample, the corresponding microwave power and N_2 flow together with other measured data including the average growth rate, obtained by dividing the thickness by the deposition time.

Table 1

Microwave power, flow of N_2 additive, and some characteristics of the samples, namely thickness, growth rate, average grain size calculated from XRD results, and the intensity ratio between the (220) and (111) diamond diffraction peaks.

Sample	Power (kW)	N_2 flow (sccm)	Thickness (μm)	Growth rate ($\mu\text{m}/\text{h}$)	Average grain size (nm)	$I_{(220)}/I_{(111)}$
ND1	3.0	1.0	29	5.4	47	4.0
ND2	3.5	1.6	40	7.1	38	3.4
ND3	4.0	1.6	45	9.6	34	6.0

SEM, micro-Raman spectroscopy and XRD analysis were used to characterize the morphology, grain size, microstructure, crystalline quality, and orientation of the diamond samples. The details of the SEM, Raman and XRD setups and measurements can be found in our previous work [20].

3. Results and discussion

For a general morphology overview, Fig. 1 shows the SEM micrographs taken from the growth surface of the three diamond samples grown at high microwave power ranging from 3.0 kW to 4.0 kW with slightly different amounts of nitrogen additive. From this figure, one can see clearly that all the samples are composed by large clusters that are constituted by finer grains. Based on this figure, one can see that when the power increases from 3.0 kW to 4.0 kW, the dimension of the fine grains remains within the nanometre scale, despite of some differences mainly on the shape of the granular structure likely to occur due to a different growth habit. Based on the morphology of our NCD films and those reported in the literature, a common feature can be summarized for NCD films: small grain size, larger clusters, no clear facet and non-defined crystallite shape. Higher magnification SEM micrographs (not shown) indeed confirm that the grain sizes are smaller than 100 nm.

Fig. 2 shows the micro-Raman spectra taken from the centre of the samples using a visible green laser of 532 nm. The appearance of the relative sharp diamond peak around 1332 cm^{-1} clearly confirms the diamond nature of all the films, although it appears mounted on a wide graphitic D band roughly at 1350 cm^{-1} , accompanying a broad band around 1500 cm^{-1} in the Raman spectra. This feature can be decomposed into two sub-bands, one at 1475 cm^{-1} and the other at about 1550 cm^{-1} , both identified by peak fitting, assigned to *trans*-polyacetylene (TPA), and the G band of graphitic materials [21], respectively. The weak band visible at 1140 cm^{-1} appearing in samples grown at higher power (3.5 kW and 4.0 kW) with slightly higher amounts of N_2 , confirm the presence of TPA at the grain boundaries, together with the 1475 cm^{-1} band [22]. It is worth to note that TPA is not intrinsic to diamond, but has been commonly found as a non-diamond impurity phase coexisting in most NCD films grown by CVD methods. It is also worth to emphasize the similarity of the typical Raman spectra of most NCD films produced either by different CVD methods or under various growth conditions [23].

In addition to Raman characterization of the optical quality of the NCD samples, the conventional XRD pattern ($\theta/2\theta$ scans) of the samples are shown in Fig. 3 in order to further study the structural properties of the films. The strongest sharp feature at 69.7° is the Si (400) diffraction peak, which comes from the single crystal Si substrate. Generally, four diamond diffraction peaks of different intensity can be seen in all the films, namely the (111) diffraction peak at $2\theta = 43.9^\circ$, the (220) at 73.5° , the (311) at 91.5° and the (331) at around 140° . The diamond (400) diffraction peak at 119.7° can be seen only in the first sample grown at 3.0 kW. A common feature for all the samples is that the diamond (220) diffraction peak appears much stronger than the (111) one, indicating a $\langle 110 \rangle$ preferred orientation. A remarkable fact is that $\langle 110 \rangle$ texture has

Download English Version:

<https://daneshyari.com/en/article/1689818>

Download Persian Version:

<https://daneshyari.com/article/1689818>

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