

Versatile properties of nanocrystalline diamond films deposited in Ar/H₂/CH₄ microwave discharges as a function of process parameters

D. Monéger¹, F. Bénédic^{*, 1}, F. Sarry², P. Renard², R. Azouani¹, O. Elmazria², F. Silva¹, and A. Gicquel¹

¹ LIMHP, UPR 1311 CNRS, Université Paris 13, 99 Avenue J. B. Clément, 93430 Villetaneuse, France

² LPMIA, UMR 7040 CNRS, Nancy University, Boulevard des Aiguilletes-BP 239, 54506 Vandoeuvre-lès-Nancy Cédex, France

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In this paper, we discuss on the versatility of nanocrystalline diamond (NCD) film properties as a function of the process parameters aiming to properly fulfil the requirements for various applications. NCD films are achieved in Ar/H₂/CH₄ microwave discharges. Their characteristics are changed by varying the deposition parameters: pulsed and continuous discharges, hydrogen concentration, microwave power, surface temperature, and N₂ ratio in the gas mixture as impurity. SEM, Raman spectroscopy, X-ray diffraction, AFM and electrical measurements (Arrhenius diagrams) are performed in order to assess the film properties. The microstructure and phase purity, that mainly determine the surface roughness, electrical resistivity, and growth rate, critical parameters for industrial applications such as mechanics and electronics, are particularly examined. The results point out the flexibility of the microwave plasma assisted process, suitable to straightforwardly control and adapt NCD film properties to the expected applications. Thus, a transition from nanocrystalline to microcrystalline structures is easily obtained with different amounts of non-diamond phases, leading to surface roughness increasing from 20 nm to 80 nm and keeping appreciable growth rates around 1 μ m h⁻¹. The most striking results concern the wide range of the film transversal resistance values measured at room temperature, evolving from 400 Ω for graphite-like NCD film to $3 \times 10^{12} \Omega$ for microcrystalline diamond.

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1 Introduction

Due to an unique combination of physical and chemical properties, such as extreme hardness, high thermal conductivity, high breakdown field, negative electron affinity, p-type doping, high acoustic wave velocity, wide optical and electrochemical windows, chemical inertness, biocompatibility, diamond is an excellent candidate for mechanical, optical, thermal, biomedical and electronic applications [1, 2]. Owing to their small grain size leading to low surface roughness and low friction coefficient, nanocrystalline diamond (NCD) films are well adapted for nanotechnological applications, micro- and nanoelectrical mechanical systems (MEMS, NEMS), surface acoustic wave (SAW) devices, as well as for conformal coatings [3, 4]. The small grain size implies a relatively large fraction of grain boundaries containing non-diamond phases, that may either deteriorate some of the extreme diamond properties or create new interesting features [5]. For instance, NCD films exhibit a low field emission threshold attributed to the presence of electron conducting channels in the grain boundaries [6], whereas an n-type conductivity of

Corresponding author: e-mail: benedic@limhp.univ-paris13.fr, Phone: +33 1 49 40 34 39, Fax: +33 1 49 40 34 14



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NCD can be induced by adding nitrogen to the deposition mixture [7]. Besides, the grain size itself may strongly influence the material properties such as the propagation losses of elastic waves [8, 9] or the

strongly influence the material properties such as the propagation losses of elastic waves [8, 9] or the tribological behaviour of the coating [10]. Thus, the film intrinsic properties (grain size, surface roughness, inclusion of non-diamond phases, ...) have to be controlled and adapted for a given application.

In the present paper, the property versatility of NCD films elaborated in $Ar/H_2/CH_4$ microwave discharges as a function of process parameters is reported. We focus on the possibility to dramatically change the film microstructure and electrical properties, starting from well-established growth conditions for NCD film and just slightly changing the deposition parameters.

2 **Experimental**

The diamond film deposition was achieved in a bell jar microwave reactor [11] using $Ar/H_2/CH_4$ feed gas. A GMP 20KED Sairem microwave power supply with a maximum output power of 2 kW, working either in pulsed or continuous mode, was used to ignite the plasma. (100)-oriented silicon samples of 1×1 cm² area, pre-treated in ultrasonic bath with a suspension of 45 µm grain size diamond powder in ethanol [12], were used as substrates. The surface temperature, controlled with an additional heating system located in the substrate holder, was measured with a bichromatic infrared pyrometer. The film thickness was monitored in real-time using pyrometric interferometry technique [13] in order to interrupt the synthesis process when approximately 2 µm were reached at the centre of the sample.

The various growth conditions employed for achieving the sample series are summarised in Table 1. Sample S1 corresponds to usual growth conditions for nanocrystalline diamond films when using argonbased gas mixture, and is taken as reference. Sample S2 was deposited in pulsed microwave discharge, samples S3 and S4 were obtained by increasing both the hydrogen ratio and the microwave power, sample S5 was achieved with very high surface temperature and finally sample S6 was completed by adding small amount of nitrogen in the feed gas. In the particular case of pulsed mode, the input power was modulated with a square wave. The frequency is related to the pulse repetition rate, the duty cycle is the ratio of the pulse duration to the pulse period, and the indicated microwave power is the peak power injected during the pulse. Moreover, it should be noted that the surface temperature may be sometimes significantly affected by the variation of the other parameters, as emphasised in Table 1. This is not critical since the effects of each individual growth parameter are clearly identified afterwards.

3 Results and discussion

The surface morphology of the samples analysed with SEM is shown in Fig. 1. Sample S1, S2 and S6 are typical of NCD films, exhibiting very smooth granular surfaces with no emerging crystallites. Sample S3 is characterised by a rougher surface with sparse coarser facetted grains emerging at the surface. The microstructure of sample S4 is characteristic of microcrystalline diamond, with a surface composed of well-facetted crystallites. A small increase of both microwave power and hydrogen ratio induces thus a

sample	pressure (mbar)	Ar/H ₂ /CH ₄ /N ₂ (%)	power (W)	temperature (°C)	frequency (Hz)	duty cycle (%)
S1	200	96:3:1:0	600	870	_	_
S2	200	96:3:1:0	1000	770	50	50
S3	200	92:7:1:0	800	930	_	_
S4	200	92:7:1:0	900	930	_	_
S5	200	96:3:1:0	600	970	_	_
S 6	200	95.6:3:1:0.4	600	870	_	_

 Table 1
 Summary of the growth condition used for the sample series.

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Fig. 1 SEM micrographs of the sample series.

drastic change in the film microstructure. Finally, graphitic lamellae are found on the surface of sample S5, which means that the deposition of sp^2 -hybridised carbon atoms was enhanced in these conditions [14].

AFM micrographs showed in Fig. 2 confirm the trends described above. The topography of each samples was estimated through the root mean square (Rms) roughness measured on a $5 \times 5 \ \mu\text{m}^2$. The results are compiled in Table 2, along with the crystalline nature of each deposited layer and growth rate estimated by pyrometric curves.

Surface roughness measured for samples S1 and S6 are typical of smooth NCD films. The best quality in terms of surface roughness is reached for sample S2 achieved in pulsed mode. Higher values are estimated between 50 nm and 80 nm for microcrystalline diamond samples (S3 and S4) and graphitised sample (S5). Table 2 also emphasises that the growth rate yielded for the various synthesis conditions remains always acceptable with values in the range $0.7-1.1 \ \mu m \ h^{-1}$.



Fig. 2 (online colour at: www.pss-a.com) AFM micrographs of the sample series.

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sample	crystalline nature	growth rate $(\mu m h^{-1})$	Rms roughness (nm)	<i>V/I</i> at 60 °C (Ω)
S1	NCD	0.9	29	2.5×10^4
S2	NCD	0.8	18	2.1×10^{8}
S3	microcrystalline-like	1	48	1.6×10^{8}
S4	microcrystalline	1.1	83	3.3×10^{12}
S5	graphite-like	0.8	57	4.2×10^{2}
S6	NCD	0.7	31	1.1×10^{5}

 Table 2
 Microstructure, growth rate, topography and electrical properties of the sample series.

The Raman spectra acquired for the sample series with a UV laser excitation (363.8 nm) are presented in Fig. 3. The spectra of sample S1, S2 and S6 are representative of NCD features with bands around 1140 cm^{-1} and 1530 cm^{-1} characteristic of trans-polyacetylene, graphite D and G bands around 1350 cm^{-1} and 1580 cm^{-1} , respectively, and a broad diamond peak at 1332 cm^{-1} [15]. When both hydrogen concentration and microwave power are increased in continuous mode, the intensity of the diamond peak drastically raises, while the signal of trans-polyacetylene bands, especially the one at 1140 cm^{-1} , decreases (S3 and S4). The Raman feature evolves then towards a microcrystalline structure. When the surface temperature significantly increases (S5), only the graphite D and G bands are observed, which is typical for highly sp²-hybridized structure [14]. Therefore, Raman spectroscopy confirms the trends appreciated through SEM and AFM.

XRD characterizations were also performed on the samples. All the XRD spectra of the deposited films exhibit the $\langle 111 \rangle$, $\langle 220 \rangle$ and $\langle 311 \rangle$ diamond diffraction peaks, which gives further evidence for the presence of crystalline diamond within the films whatever the growth conditions.

Finally, the electrical characterisation of the sample series was carried out with a four point device. This system enables the measurement of the electrical resistivity using the Van der Pauw method [16]. Since the four point method is not adapted for the determination of the film intrinsic resistivity in the case of thin resistive layers, such as diamond, deposited on conducting substrates, such as the doped silicon wafer used in this work, only the transversal resistance of the diamond/silicon system was measured. This resistance is proportional to the film resistivity, and for samples of similar thickness, it indicates the evolution of the electrical properties of the deposited layer. In this configuration, a voltage V is applied between the external faces of the sample and the crossing current I is measured. The ratios V/I were thus estimated as a function of the sample temperature, for a range from room temperature to 750 K and under pressure lower than 10^{-6} mbar. The data acquisition was performed during the cooling step in order to





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Fig. 4 Arrhenius diagram of the sample series.

avoid the influence of the desorption processes usually observed during the heating procedure, and generally due to conductive hydrogen layer [17]. The Arrhenius diagrams thus obtained are presented in Fig. 4. The V/I values recorded at almost room temperature (≈ 60 °C) are also given in Table 2.

The results show that the transition from conventional NCD (S1) to microcrystalline-like NCD (S3) and microcrystalline diamond (S4) films is associated to a wide increase of the V/I ratio by about 8 orders of magnitude at 60 °C, with values evolving from $\approx 10^4 \Omega$ to $\approx 10^{12} \Omega$. This could be attributed to the diminution of the grain boundaries composed of partially π -bonded carbon species due to the increase of the grain size. On the contrary, the film graphitization observed when the surface temperature is increased (S5) leads to a significant reduction of the V/I ratio at room temperature down to $\approx 400 \Omega$, which can be attributed to the enhanced formation of conductive non-diamond carbon species. Therefore, the resistance values for samples S1, S3, S4 and S5 are in good agreement with the film purity as investigated by Raman spectroscopy (Fig. 3). Compared to the reference sample (S1), the introduction of small amount of nitrogen in the feed gas (S6) provokes a noticeable increase of the resistance by a factor 10 to 100 for the range of temperature explored. This result could be attributed either to a basic difference in the film thickness, or to a complex competition between the effects of possible nitrogen-related centres located on the diamond surface or in the diamond grain boundaries [18]. Indeed, it has been reported that nitrogen-vacancy related complex may act as a shallow donor centre, whereas the complexes of nitrogen and dangling bond or nitrogen with a π -bond may play the role of compensation centres [19]. The most striking result is the behaviour noticed for the sample achieved in pulsed discharge (S2), which presents, although its NCD nature, the same Arrhenius plot than microcrystalline-like sample (S3). This could be attributed to a higher purity resulting either from a change in the growth mechanisms allowed by the use of a pulsed plasma, or to the decrease of the surface temperature during the synthesis (Table 2). This important result demonstrates that it is possible to synthesize NCD film in Ar/H₂/CH₄ microwave discharges with acceptable growth rate, small grain size and surface roughness, and electrical resistivity compatible with applications requiring low surface conductivity such as SAW devices [1].

4 Concluding remarks

In this paper, we discussed on the flexibility of NCD film properties as a function of the process parameters aiming to fulfil the requirements for potential applications. Starting from usual growth conditions employed for $Ar/H_2/CH_4$ microwave discharges, the growth parameters were slightly changed and the characteristics of the deposited films were investigated with conventional surface analysis techniques and

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four point method. The results demonstrate the versatility of NCD film properties in terms of microstructure, topography, purity and therefore electrical resistivity. A minor increase of both microwave power and hydrogen concentration provokes a sharp transition towards microcrystalline features. An increase of the deposition temperature leads to a consequent graphitization of the films. The use of a pulsed discharge leads to a lower surface roughness and to electrical characteristics close to those of microcrystalline-like NCD film. The addition of small amount of nitrogen in the feed gas does not affect the film morphology but the electrical resistance is increased by at least a factor of 10. Eventually, keeping an appreciable growth rate of around $1 \,\mu m \,h^{-1}$, the transversal resistance obtained for the sample series varies from 400 Ω to $3 \times 10^{12} \,\Omega$, while the film microstructure and topography evolves from graphitelike to microcrystalline-like. This points out the flexibility of the microwave plasma assisted process, suitable to easily control and adapt NCD film properties to a given application. Further works are now in progress in order to study more accurately the effects of pulsed microwave discharges on the plasma reactivity and the effects of the incorporation of small amount of nitrogen in NCD films containing H-atoms.

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