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Nanocrystalline diamond films grown at very low substrate temperature using a distributed antenna array microwave process: Towards polymeric substrate coating

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ABSTRACT

The growth of NanoCrystalline Diamond (NCD) films at very low substrate temperature on large area surface using a distributed antenna array (DAA) microwave reactor operating in $H_2/CH_4/CO_2$ gas mixture is investigated. The estimated activation energy is in the range 1.3–3.2 kcal·mol^{-1} depending on the injected microwave power and resulting substrate temperature range, which is comparable to values reported for other low-temperature NCD growth processes. The ability of the DAA reactor to deposit NCD films at a surface temperature down to 130 °C is demonstrated. NCD films composed of nanometric grains of 4.5 nm with a surface roughness of 27 nm are thus obtained, with a growth rate of 5 nm·h^{-1}. The decrease of the deposition temperature is followed by an increase of the renucleation rate leading to a reduction of the grain size and to a subsequent promotion of non-diamond phases. At this temperature, the decrease of the CH_4 percentage in the feed gas permits to improve the film purity but leads to a drastic decrease of the growth rate down to 2.5 nm·h^{-1}. Finally, a successful attempt of NCD film deposition on polytetrafluoroethylene (PTFE) substrate is shown aiming at exploring the coating of temperature-sensitive polymeric substrates employed for biomedical applications.

1. Introduction

Diamond is an excellent candidate for mechanical, optical, thermal, biomedical and electronic applications [1]. More specifically, Nanocrystalline Diamond (NCD) films have been the subject of an increasing interest for the last 20 years because of their very low thickness-dependent roughness and specific properties resulting from the nanometer-scale grain size and relatively large fraction of non-diamond phases localized at grain boundaries [2]. Combining suitable properties such as surface smoothness, high hardness, low friction coefficient and biocompatibility, NCD is one of the emerging materials for micro- and nano-electrical mechanical systems (MEMS, NEMS), surface acoustic wave (SAW) devices and biomedical applications [3]. For example, the implantation of NCD coated orthopedic screws into a human organism was successfully demonstrated without transplant rejection [4].

However, some of these applications require substrates that are temperature-sensitive with most of time a very low melting temperature. This is the case for polytetrafluoroethylene (PTFE), more and more used for biomedical applications such as bone regeneration or cardiovascular engineering [5,6], which has a melting point of 330 °C. Besides, combination of PTFE with Diamond-Like-Carbon (DLC) or NCD films showed an improvement of its functional properties, for example in the case of interactions with human osteoblastic cells [7,8]. Therefore, the development of new NCD synthesis processes operating at low deposition temperature is needed in order to avoid substrate damages and property modifications during growth. Furthermore, industrial scale applications necessitate deposition processes compatible with large area treatment.

Recently, in order to unlock technological obstacles and explore the coating of novel and innovative substrates, new deposition microwave reactors working at low temperature (typically lower than 500 °C) and on large area (from 20 × 20 to 30 × 30 cm^2) emerged, using $H_2/CH_4/CO_2$ gas mixture [9–12]. In the particular case of the high plasma density Distributed Antenna Array (DAA) reactor [13], low temperature NCD growth was demonstrated down to 250 °C on silicon and silicon nitride (Si_3N_4) substrates [14]. Thus, in order to allow the treatment of other temperature-sensitive substrates, the growth process using such a reactor has to be considered and optimized for deposition temperature lower than 250 °C.

In this paper, we investigate the aptitude of the DAA reactor for growing NCD films at very low substrate temperature down to 130 °C. Firstly, the effects of the deposition temperature on the characteristics of the films synthesized on silicon substrates, such as surface roughness, morphology, microstructure and growth rate, are assessed. Secondly,

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the influence of the gas mixture composition is examined at very low deposition temperature. Finally, a first attempt of NCD layer deposition on polytetrafluoroethylene (PTFE) substrate at 130 °C in optimized growth conditions is presented.

2. Experimental

Full description of the low temperature and large area deposition DAA reactor has already been given elsewhere [12]. Succinctly, the DAA reactor consists of 16 coaxial plasma sources arranged in 4 × 4 matrix fed by a 6 kW microwave generator working at 2.45 GHz. Discharges are ignited around each elementary source in $H_2/CH_4/CO_2$ feed gas and form uniform plasma which diffuses to the substrate. The temperature of the substrate is monitored by a thermocouple located in the 4-inch molybdenum substrate holder, very close to the backside of the substrate, and controlled with a graphite resistor through a PID regulator. For a good thickness homogeneity, *i.e.* deviation less than 10%, the distance between the elementary sources and the substrate is fixed at 95 mm. Polished (100) silicon wafers with thickness around 550 μm (n-type, 5–10 $\Omega \cdot cm^{-1}$, semiconductor grade) of 4-inch diameter are used as substrates. Prior to the growth step, the wafers were cleaned in acetone and rinsed in ethanol, and then seeded by spin coating with 25 nm nanodiamond particles in colloidal solution [15]. The standard growth conditions are characterized by a gas pressure of 0.35 mbar, a total gas flow rate of 50 sccm and a feed gas composition of 96.5%/2.5%/1% for $H_2/CH_4/CO_2$ precursors. These operating conditions allow the synthesis of diamond films down to 400 °C, with nanocrystalline features characterized by a surface morphology showing non-faceted particles with a grain size in the range 10–20 nm and a thickness-independent surface roughness typically around 10 nm [12]. For these reasons diamond films elaborated in the DAA system are designated as NCD films.

In the first part of this study we aim at investigating the ability of the DAA reactor for NCD film growth at very low surface temperature in the range 100–400 °C. In absence of a cooling system the only way to significantly decrease the substrate temperature is to turn off the heating system and to decrease the injected microwave power. A surface temperature between 130 and 300 °C can be then reached when the heating system is off for a microwave power varying between 1.2 and 3 kW. The microwave power and the resulting substrate temperature for samples achieved as a function of the deposition temperature in standard conditions are reported in Table 1 (samples A–D). For each microwave power employed, the effect of a variation of the substrate temperature in a range 300–400 °C on the growth rate is also investigated by switching on the additional heating system and varying the current intensity passing through the graphite resistor.

In the second part of the paper, the effects of the CH_4 concentration decrease are investigated at 130 °C in order to improve NCD film quality. In comparison with sample D, the CH_4 percentage was fixed to 1.5 and 1% for samples E and F, respectively (Table 1).

Finally, in the last part the NCD growth on polytetrafluoroethylene (PTFE) polymeric temperature-sensitive substrates, prepared by using the *ex situ* pretreatment described above, excepted acetone rinsing, is examined at 130 °C in the growth conditions of sample D (Table 1, sample G).

Table 1
Sample deposition conditions.

Sample name	Substrate	Power [kW]	Temperature [°C]	H_2 [%]	CH_4 [%]	CO_2 [%]
A	Silicon	3	400	96.5	2.5	1
B		3	300			
C		2	230			
D		1.2	130			
E	Silicon	1.2	130	97.5	1.5	1
F		1.2	130	98	1	1
G	PTFE	1.2	130	96.5	2.5	1

The deposition duration was set between 4 and 23 h, depending on growth conditions, in order to obtain continuous films with thicknesses around 100 nm.

The film morphology was investigated by top-view Scanning Electron Microscopy (SEM) images taken by a field emission ZEISS ULTRA plus SEM system. Surface roughness was measured with a VEECO Dimension 3100 Atomic Force Microscopy (AFM) system in tapping mode in air.

The Raman spectra were obtained with a HR800 (HORIBA Jobyn-Yvon) working in a confocal mode and in the back-scattering configuration, using a continuous-wave diode-pumped solid state laser (CoboltblueTM) at 473 nm as an excitation source with a power of 50 mW. The quality of the deposited films may be roughly estimated from deconvoluted Raman spectra through the sp^3 fraction defined as:

$$sp^3(\%) = 100 \cdot \left(\frac{60 \cdot I_{\text{diamond}}}{60 \cdot I_{\text{diamond}} + \sum I_{\text{non diamond}}} \right) \tag{1}$$

where I_{diamond} is the Raman diamond peak area at 1332 cm^{-1}, which represents sp^3 phase, and $\Sigma I_{\text{non diamond}}$ is the sum of Raman non diamond peak areas. A Raman signal efficiency factor averaged ratio of 60 between non diamond and sp^3 phases, mainly weighted by the response of the graphite G band centered at 1580 cm^{-1}, was used for the considered excitation wavelength.

X-Ray Diffraction (XRD) patterns were obtained using $CuK_{\alpha 1}$ radiation ($\lambda = 1.54056$ Å) with an incident angle of 1°. The grain size was estimated using modified Scherrer equation applied on the (111) and (220) diamond diffraction peaks [16]. Film thickness was measured by three methods: *(i)* UV–visible reflectometer (NanoCalc, Ocean Optics), *(ii) in situ* visible interferometry, and *(iii)* weight gain measurement after growth.

3. Results and discussion

Previous plasma investigations have pointed out a limited dependency of some process key-species densities such as CH_3, C_2H_2, CO and H, measured at the substrate position as a function of the injected microwave power in the range 2–3 kW [17]. In the same time, the gas temperature measured through H_2 molecule emission significantly decreases from 700 to 400 °C when the microwave power decreases from 3 to 1 kW [18]. The diminishing of the gas temperature thus leads to a significant reduction of the substrate temperature without requiring additional cooling system so that 130 °C can be reached for 1.2 kW.

For the three microwave powers reported in Table 1, *i.e.* 1.2, 2 and 3 kW, the effects of the substrate temperature were first investigated on the growth rate in order to allow comparisons of the process activation energy according to the following Arrhenius equation:

$$G = G_0 \exp(-E_a/RT) \tag{2}$$

where G is the growth rate, G_0 is a temperature-independent constant, E_a is the activation energy, R is the universal gas constant ($1.989 \text{ cal} \cdot K^{-1} \cdot mol^{-1}$) and T is the substrate temperature.

The Arrhenius diagram of the growth rate estimated for the films grown at 1.2, 2 and 3 kW for a temperature range of 130–400 °C, 230–600 °C and 300–600 °C, respectively, are given in Fig. 1. According to Eq. (2), the activation energy derived from the gradient of a least-square fitting of the growth rate values are $E_a^{1.2 \text{ kW}} = 1.3 \pm 0.2 \text{ kcal} \cdot mol^{-1}$, $E_a^{2\text{-kW}} = 1.46 \pm 0.15 \text{ kcal} \cdot mol^{-1}$ and $E_a^{3 \text{ kW}} = 3.2 \pm 0.2 \text{ kcal} \cdot mol^{-1}$.

It should be reminded here that a single activation energy should be ideally related to a one-step reaction leading to the growth process and characterized by a single activation barrier. For the considered experimental conditions, no thorough reaction scheme describing all NCD