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Early stages of diamond growth on substrates with different carbon diffusivity

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ABSTRACT

In this work, nanocrystalline diamond was deposited with a direct-current micro-plasma device on substrates with different carbon diffusivity. No substrate pre-treatment was performed and the same deposition conditions were adopted for all substrates, with the intention to investigate the first stages of growth. Samples were grown with increasing deposition time. Scanning electron microscopy and visible Raman spectroscopy were used to derive morphological and structural information. The growth dynamics was found to be the same on all substrates, with the deposition of a graphite layer prior to diamond growth. This layer was extensively characterized and a link between the structure and morphology of this layer and the subsequent features of the diamond grown on it was found. Moreover, diamond tens of micrometers thick was deposited in few hours, opening the possibility of producing diamond samples of practical interest. Particularly, the growth of nanocrystalline diamond on iron without substrate pre-treatment or interlayer deposition is reported, showing the feasibility of depositing diamond even on ferrous materials.

1. Introduction

Due to its outstanding properties, diamond possible applications broadened in many fields beyond the luxury industry [1–3]. This led to an increased global interest for diamond laboratory synthesis, with the aim to find out the main influencing parameters governing the deposition process and produce a valuable material. Chemical vapor deposition (CVD) techniques are nowadays the main industrial processes exploited to obtain synthetic diamond [4–6], especially at a laboratory scale. In particular, plasma-enhanced chemical vapor deposition (PECVD) techniques attract great interest because of the high growth rate and chemical purity of the deposited material [7]. Both single-crystal and polycrystalline diamond films can be produced: particularly, polycrystalline films have several interesting properties and less requirements on technical aspects related to the deposition process with respect to the single-crystal one. Moreover, the possibility to produce diamond in the form of coating preserving bulk diamond properties pushed forward the research of diamond laboratory synthesis.

Nevertheless, many difficulties afflict diamond films synthesis. One of the main difficulties derives from the choice of the substrate material. The possibility to grow diamond films on different substrates would be of interest for several applications, e.g. high power electronic, high frequency devices, UV–Vis-IR windows, wear resistance coatings and solid state detectors. However, having a high surface energy with respect to other materials, growing diamond on substrates different from diamond itself is anything but trivial [8]. Substrate materials suitable for diamond growth can be organized into three main families, depending on carbon/surface interaction and carbon diffusivity, namely [9,10]: materials having a little or no solubility or reaction with C, e.g. copper, silver and gold, materials in which carbon easily diffuses or dissolves or with a weak carbide formation, e.g. platinum, palladium, rhodium, nickel and iron, and materials with strong carbide-formation tendency, e.g. titanium, molybdenum, tungsten and silicon. Moreover, it is widely believed that nucleation of diamond on non-diamond substrates usually occurs via an intermediate non-diamond based layer [11,12]. This layer may be the result of the interaction with the substrate during the deposition process, since carbon atoms from the plasma can diffuse in the substrate material, saturate it and then act as preferential nucleation sites. To date, diamond films have been grown on carbide layer [13,14], graphite [15,16], diamond-like amorphous carbon and carbon oil [17–19]. Even if the theory of diamond growth mechanism is nowadays widely agreed, several contrasting observations on what happens in the nucleation phase on substrates even of the same family can be found in literature. For instance, both graphite, amorphous carbon and carbide compounds have been identified as the main responsible for diamond nucleation on carbide-forming materials

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Table 1
Value of carbon diffusivity in different substrate materials, calculated at 800 °C. For Rh, no available data are found.

Substrate	Si	Mo	W	Fe	Ni
Carbon diffusivity [$cm^2\,s^{-1}$]	$7\cdot10^{-15}$	10^{-11}	10^{-13}	$8\cdot10^{-7}$	$2\cdot10^{-8}$

[17,20,21]. In addition, substrate pre-treatments such as scratching, biasing or substrate coating are often used in order to enhance diamond nucleation density, and to control the grown morphology, texture and quality of the diamond films [22–24].

In a previous work [25], the authors already showed how the deposition of nanocrystalline diamond with a peculiar PECVD technique, i.e. the direct-current micro-plasma device (DC-μP), on carbide-forming substrates such as silicon (Si) and molybdenum (Mo), proceeds towards the formation of an intermediate graphite layer. An explanation of the diamond growth dynamics in the early stages of the deposition has been provided, in accordance to diamond growth mechanism. Indeed, even if such peculiar technique has already been proved to be particularly interesting for diamond deposition [26], no in-depth and systematic study has already been performed with the DC-μP on the dynamics of diamond growth on different substrates. Considering these results, a natural development is to extend the investigation to other family of substrates where other mechanisms of growing could be invoked to explain the diamond growing.

In this work, nanocrystalline diamond films have been grown on different substrate materials, with the same deposition apparatus and process conditions found in [25]. With the intention to deeply investigate the growth dynamics especially in the early stages of growth, materials with a diffusivity with carbon different from the case of Si and Mo were chosen. Additionally, only conductive substrates were chosen because of the limit linked to the plasma generating system, which is based on a direct current source. Tungsten (W), iron (Fe), nickel (Ni) and rhodium (Rh) were used in this work. W was chosen, because of its carburizing tendency as Mo and Si, but with a lower value of the Gibbs free energy of formation of the respective carbide [27]. Ni and Fe because of their high diffusivity with carbon. Moreover, even if both Ni and Fe have a carbide form, at the pressure and temperature deposition conditions used in [25], that are the same adopted for this work, no carbide compound should form [27]. Regarding Rh, the substrate used in this work is a 1 μm film of nanostructured columnar Rh grown with a pulsed laser deposition technique on Si [28]. Values of carbon diffusivity of the exploited substrates can be found in Table 1, as derived from [7].

The investigation of diamond growth was pursued depositing different spots with increasing deposition time. A characterization procedure similar to [25] combining SEM and Raman spectroscopy was adopted, whose potentiality has already been shown. Particularly, in the previous work a multi-wavelength Raman analysis has been performed, addressing structural information in an original and complete way. Since the aim of this work is to focus on what happens in the early stages, this time only visible Raman spectroscopy was used for structural characterization, and scanning electron microscopy (SEM) was used to derive the main morphological information about the grown samples.

2. Experimental technique

The deposition apparatus is schematically depicted in Fig. 1.

It consists of an in-house designed vacuum chamber of stainless steel, a plasma generating system and a gas supply system. The main feature of this experimental set-up is the stainless-steel column with 178 μm inner diameter capillary tube, acting as the micro-hollow cathode allowing the gas inlet used to create the flow-stabilized micro-plasma jet. All technical aspects related to such device and its configuration have already been addressed in [25]. The carbon source is methane gas mixed with hydrogen, with fluxes of 0.5 sccm and 100 sccm respectively. Substrates are previously cleaned with a sonic bath in hexane and deionized water, then placed under vacuum in the deposition chamber for several hours. No substrate pre-treatment is performed. Diamond was grown on all substrates increasing time from few minutes to hours. The deposition conditions are summarized in Tables 2 and 3.

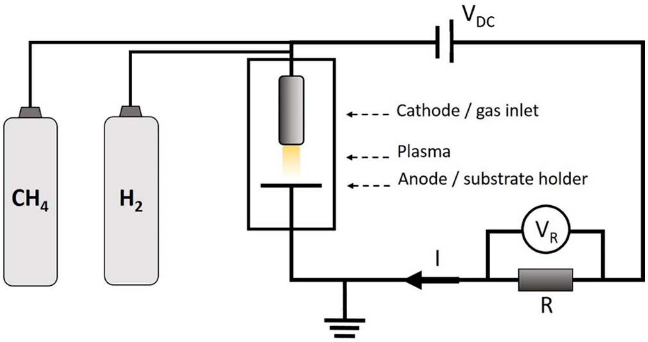

Fig. 1. Schematic representation of the direct-current micro-plasma device.

Table 2
Range of operating conditions for diamond deposition with DC-μP.

Substrates	Mo, Si, W, Ni, Fe, Rh
Temperature	960 °C
Pressure	200 Torr
Φ_{CH4}/Φ_{H2}	0.005
Supply voltage	610 V
Plasma current	10–12 mA

SEM micrographs are taken using a ZEISS Supra 40 scanning electron microscope with an accelerating voltage of 5 kV. Visible Raman spectroscopy is performed at room temperature by a Renishaw InVia micro-Raman spectrometer equipped with an Ar laser, using the blue line (457 nm, 2.71 eV). The spectral resolution is about 3 cm^{-1}.

3. Results and discussion

All samples were grown with increasing deposition time, from few minutes to hours. SEM and Raman measurements were performed for all deposition times, and many similarities were found on all substrates, as in the previous work [25]: small and isolated agglomerates with different geometrical shapes are found in the first minutes, that grow both in dimensions and numbers as the deposition time increases, until coalescence in a nearly homogeneous deposition. Raman spectra change shape as the deposition time increases, showing a predominant graphitic signal for the early minutes of growth that disappears as the agglomerates coalesce in a continuous deposit, and at this point typical features of nanocrystalline diamond are found. In the following, only samples grown at 5 min and 30 min are shown. Particularly, 5 min were chosen because illustrative of the early stages of growth. 30 min were chosen since, as shown in the following, at this time a nearly homogeneous deposit was found on almost all substrates.

SEM images of the depositions on Mo, Si, W, Ni, Fe and Rh are

Table 3
Substrates used for diamond deposition and deposition times.

Substrates	Deposition time
Mo	2.5 min, 5 min, 10 min, 15 min, 30 min
Si	7 min, 15 min, 30 min, 1 h, 2 h
W	5 min, 15 min, 30 min, 1 h
Ni	5 min, 15 min, 30 min, 1 h
Fe	5 min, 15 min, 30 min, 1 h
Rh	5 min, 15 min, 30 min, 1 h