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The valuable role of renucleation rate in ultrananocrystalline diamond growth

D.C. Barbosa [a,*], P. Hammer [b], V.J. Trava-Airoldi [a], E.J. Corat [a]

[a] INPE, Instituto Nacional de Pesquisas Espaciais, LAS, CP 515, 12227-010, São José dos Campos, SP, Brazil
[b] UNESP, São Paulo State University, Institute of Chemistry, 14801-970 Araraquara, SP, Brazil

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ABSTRACT

This is a comprehensive study of the ultrananocrystalline diamond renucleation rate. The films deposited in a hot-filament chemical vapor deposition system (HFCVD) used an argon rich environment (90 vol.%), known as ideal for ultrananocrystalline diamond deposition. Substrate temperature (750 °C), total pressure (30 Torr) argon flow rate (180 sccm) were constant in all experiments. Methane concentrations of 0.25, 0.5, 1, 1.5 and 2 vol.% balanced with hydrogen to a total flow rate of 20 sccm. Scanning electron microscopy (SEM) let morphology inspection. Visible-Raman scattering leaded to estimating relative influence of sp^2 bonds. X-ray photoelectron spectroscopy (XPS) measured the chemical bonds distribution. X-ray diffraction assessed crystallinity and diamond renucleation rates. The increase in methane content in the gas mixture promotes morphology changes from micro (faceted), to nano (cauliflower), and to ultrananocrystalline (ballas-like) diamond. It reaches a lamellar graphitic structure at the higher methane concentration. This transition is concurrent with: a decrease of film specific mass, an increase of diamond renucleation rate, an increase of sp^2 phase content, as seen by Raman spectroscopy and, an increase of C–H bond associated with C–C bond, as measured by x-ray photoelectron spectroscopy. Renucleation shows up as a very important process that presents a quadratic correlation with $[CH_4]$ in the feed gas. This new result may help bridging MCD, NCD and UNCD into a single understanding of diamond growth.

1. Introduction

Chemical vapor deposition diamond thin films may present different morphologies, like microcrystalline diamond (MCD), nanocrystalline diamond (NCD) and ultrananocrystalline diamond (UNCD). MCD consists of micron sized grains, ranging from one to hundreds of micrometers of pure and crystalline sp^3 bonded carbon. NCD is a thin diamond film grown with a high nucleation density (in the order of $10^{11}/cm^2$) [1,2]. Its crystallite size and roughness increases with the film thickness [1,3]. UNCD is a fine grain material, 3–5 nm, with abrupt grain boundaries, grown with a high renucleation rate without columnar growth habits [1,3,4]. Therefore, its surface roughness is independent of film thickness [1,4]. UNCD films growth by Hot-filament chemical vapor deposition (HFCVD) uses gas phase with a small quantity of a hydrocarbon in a mixture of hydrogen in a high volume ratio of argon. Other gas mixtures with the introduction of other noble gasses and nitrogen, or gas mixtures of only hydrocarbons with hydrogen, but at relatively high hydrocarbon content, may also promote UNCD growth [14,37]. These films have been subject of a large interest in the scientific community, motivated by their extraordinary properties for tribological, mechanical, biomedical and electronic applications [4–6]. This interest is especially because of the high surface smoothness, electron field emissivity, as well as its ability to incorporate n-type dopants [7–9]. With all this potential, the UNCD became object of many studies for several applications.

The behavior of diamond crystallite size decreasing down to nanometer scale has been subject of many studies [10–14]. A major advance achieved was adding inert gas, usually argon, into typical microcrystalline deposition conditions. These findings provided a route to control the microstructure of the diamond film, leading to thick and smooth nano and ultrananocrystalline film. Even though argon addition is a broad practice to develop many applications, the changes in the surface morphology and growth conditions occurring during the ultrananostructured diamond deposition still deserves further studies. The question of why UNCD grows at this condition has been subject of many discussions [2,4,10,12–18]. This is the main subject of this work, which gives special attention to renucleation process.

Many publications have reported the influence of methane feed in the gas phase for MCD growth [19–23]. For an environment with excess argon, ideal for diamond UNCD growth, there are some publications [24,25] but the subject is still open. In both cases the increase of sp^2 carbon phases shows up with increase of methane content in feed gas [19,22–25]. However, most works focus only the graphitization without specifying the structural and morphological changes compared to gas-phase of deposition environment. This is an interesting point because a comprehensive study of these transitions can be used for not only

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[*] Corresponding author at: MCT, INPE, Circuito Impresso, Av dos Astronautas, 1758, Jd. Granja, São José dos Campos, SP, CEP: 12227-010, Brazil. Tel.: +55 12 32086905; fax: +55 12 32086717.
E-mail addresses: divani@las.inpe.br (D.C. Barbosa), corat@las.inpe.br (E.J. Corat).

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explaining the differences observed in the morphology as also for proponent applications of these samples and the ideal growth conditions.

This work presents detailed insights on the structure and morphology with focus in the transition from faceted, to nano and to ultranano diamond, up to lamellas of graphite. These films were analyzed by scanning electron microscopy (SEM), Raman scattering spectroscopy, x-ray photoelectron spectroscopy (XPS) and high resolution x-ray diffraction. These analyzes show that upon increasing methane content in feed gas it follows the decrease of deposited film specific mass, the increase of sp^2 carbon bonds ratio, the increase of C–H bond associated with C–C bond, and the increase of diamond renucleation rate. The comparison with gas phase models shown in literature indicates no correlation among growth species and growth rate dependence on methane content in feed gas. Besides, the renucleation rate presents an excellent correlation with [CH$_4$] in feed gas. These results suggest renucleation as a very significant process during diamond growth.

2. Experimental

The samples were deposited in a conventional HFCVD reactor with five straight 125 μm diameter tungsten filaments. The experimental apparatus has independent substrate temperature control adjustable up to 750 °C at a total pressure of 30 Torr. Methane and hydrogen concentrations were the only parameters changed in all experiments. The feed gas mixture varied with 0.25, 0.5, 1, 1.5 and 2 vol.% methane balanced with hydrogen and 90 vol.% argon. Filaments temperature was 2200 °C as checked by an uncorrected disappearing filament pyrometer. The distance between the filament and substrate was 5 mm and the typical deposition time was 8 h.

Silicon wafers (100) and freestanding diamond pieces were the substrates. The films deposited on silicon substrate served for morphological and structural characterization. Silicon substrates were pretreated in an ultrasonic bath with a 250 nm diamond powder suspension in hexane, during one hour, and then cleaned in acetone during five minutes. The films deposited on diamond substrates served to measure the mass growth rate The diamond substrates were previously grown on graphite in a conventional microwave plasma reactor (2.45 GHz) using a gas mixture of 3 vol.% methane and excess of hydrogen. They were removed from the graphite substrate and treated with sulfocromic solution to remove the graphite residues. Mass growth rate was obtained by weighting the diamond substrate before and after growth in the HFCVD reactor. The area of each diamond substrate was measured.

Scanning electron microscopy (SEM) images, got in a JEOL JSM-5310 microscope, showed the surface morphologies and the cross sections of the films grown on silicon. Cross section images showed film thickness and growth behavior. Raman scattering spectroscopy of the samples used a 514.5 nm laser excitation in a Renishaw microscope System 2000. The ratio of the relative intensities of graphite G and D bands (I_D/I_G) estimated the graphitic structure present on samples. The crystallographic analysis in a Philips PW-1840 difractometer allowed measurements of diamond crystallite size to estimate renucleation rate. The XPS analysis showed the compositional changes on surface region of the deposited specimens. These analyzes were carried out at a pressure of less than 10^{-6} Pa using an UNI-SPECS UHV spectrometer, with the Mg Kα line ($h\nu = 1253.6$ eV) and with the analyzer pass energy set to 10 eV. Spectra fitting used Shirley's method to subtract the inelastic background of the C 1 s electron core-level. It also used no constraints with multiple Voigt profiles. Binding energies corrections used the hydrocarbon component of adventitious carbon fixed at 285.0 eV. The width at half maximum (FWHM) varied between 1.0 and 1.8 eV and the estimated accuracy of the peak positions was ±0.1 eV.

3. Results and discussion

Fig. 1 shows the SEM images with sample surface morphology and the respective cross-sections as inset. This figure reveals a dramatic change on the morphology of films deposited at different methane concentration in the feed gas. The samples change from faceted microstructures, pass through cauliflower to ballas-like diamond morphology, and finally come to lamellar graphitic morphology. The sample prepared at 0.25 vol.% methane in feed gas presents typically faceted diamond microstructures with columnar growth (Fig. 1a). For 0.5 vol.% methane in feed gas a “cauliflower” nanodiamond morphology appeared, related to a high renucleation rate. The 1 and 1.5 vol.% methane in feed gas (Fig. 1c and d) films presents ballas-like ultrananocrystalline diamond morphology, consisting of extremely fine grained coalescent crystallites. The cross-sectional view does not display a columnar growth, typical of microcrystalline diamond, but rather a granular structure with abrupt grain boundaries, typical of ultrananocrystalline diamond. Finally, for 2 vol.% methane in feed gas a typical nanographite film with lamellae structure formed [23].

Fig. 2a shows the growth rate and film specific mass dependence with methane content in the feed gas. Two growth rate dependences are shown. The first one is the thickness growth rate, calculated by the cross-section shown in the Fig. 1 divided by the growth time. The second one was calculated by measuring mass growth rate and considering the diamond specific mass (3.52 g cm^{-3}) to calculate the growth rate. This figure evidences the great difference in the behavior of thickness and mass growth rates. The specific mass shown in Fig. 2b was calculated as the ratio between the values of mass and thickness growth rates. It further evidences the differences in both growth rates. It decreases with methane concentration in feed gas, ranging from values close to diamond (3.5 g cm^{-3}), at low methane concentration to values close to graphite (2 g cm^{-3}). While specific mass drop close to 2 g cm^{-3} of the graphite film (2 vol.% CH$_4$) was expected, the decrease shown in Fig. 2b, mainly for the 1 vol.% CH$_4$, is a new result. Most authors consider constant specific mass to measure thickness growth rate as the real film growth rate [19–24]. However, Barbosa et al. [3,25] have already shown that mass growth rate is the best choice in a so transitional region. Either sp^2 and CH co-deposition, voids formation and defective structures because of a high renucleation rate may all induce a lower specific mass. Examining Fig. 1c the transition to ballas-like structure leaves many voids around the grains, which is the most likely reason for the reduction in specific mass at this point. The error bars shown in Fig. 2a are result of three experiments in same conditions. The larger deviation also comes out in thickness growth rate for 1 vol.% CH$_4$. This is indicative of a very transitional region. Mass growth rate does not reflect it.

The first order Raman spectra, Fig. 3, presents: (i) the 1332 cm^{-1} peak that matches the line from bulk diamond, the signature of sp^3 bonded carbon [26]. (ii) The 1350 cm^{-1} of disordered graphitic D band, that is related to defective sp^2 carbon sites [26,27]. (iii) The 1580 cm^{-1} of graphite G band, a signature of sp^2 structures [26,27]. And the 1150 and 1450 cm^{-1} bands, both assigned to the transpolyacetylene segments at grain boundaries, a compound typically found in NCD [28].

Raman spectra also show dramatic changes with methane in feed gas. The characteristic first order Raman peak from bulk diamond at 1332 cm^{-1} is present only with 0.25 vol.%. This suggests a preferential sp^3 bonded material. With methane insertion it is possible to see a decrease of diamond band intensity with the increase of graphitic bands. For 0.5 vol.% the spectra show the presence of transpolyacetylene structure as well the graphite G and D bands. The D band is so intense that masks the 1332 cm^{-1} diamond peak. These spectra are characteristic of NCD films [1]. Similar spectra were obtained for samples prepared at 1 and 1.5 vol.% methane (Fig. 3c and d). They show more intense D in comparison to G band, and the transpolyacetylene band shows up only as a small shoulder. This