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Surface characterization of NCD films as a function of sp^2/sp^3 carbon and oxygen content

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ABSTRACT

The wettability of nanocrystalline diamond was systematically studied using water by sessile-drop method for films grown with different concentrations of methane addition in the $Ar/CH_4/H_2$ mixtures. These films showed diamond grains agglomerate, also called ballas diamond, which presented a decrease on film roughness from 230 to 12 nm associated to a contact angle decrease from 97° to 73°, as the methane concentration increased from 0.5 to 2.0 vol.%. Considering the wettability evolution is only due to a chemical surface modification, it could be reasonably proposed that the progressive loss of the hydrophobic character is linked to the progressive increase of surface terminations with oxygen (carbonyl or carboxyl). This result is coherent with the observed from the deconvolution of XPS spectra, where the total oxygen amount increased from 5 to 14% and the sp^3/sp^2 carbon ratio decreased from 7.6 to 6.9 as the methane concentration increased. Moreover, the stress behaviour, analyzed by Raman spectroscopy, was explained pointed out the nanodiamond/nanographite transition process due to the methane increase in the gas phase.

1. Introduction

Nanocrystalline diamond (NCD) films have appeared as a new material for different applications, mainly in electrochemistry. However, the growth of NCD films presents scientific and technological challenges that are crucial for their application. Particularly, for some application where the film contacts with a liquid medium, the diamond wettability is very important. While wetting of microcrystalline diamond CVD films has been extensively studied [1–5], wettability of NCD films did not attract much attention so far. Nevertheless, considering the diamond grains themselves in the ultra/nanocrystalline diamond films which contain many structural defects, one can expect to observe some peculiarities in wettability of nanocrystalline films compared to that of microcrystalline films and monocrystalline diamond [6,7].

Furthermore, this method is easy to use and provides more information about crystallographic structure of the surface also correlated to the chemical nature of the surface functional groups associated to their variation in contact with different liquid media. Besides, the wettability measurements allow evaluating the surface energy values [3]. In case of ultra/nanocrystalline diamond films, the fraction of atoms at the grain boundaries is fairly large and contains disordered bonds, sp^2-hybridized carbon atoms, hydrocarbons and impurities [8–10] that may influence on wettability and electrodes electrochemistry response of nanocrystalline films [9,11]. The presence of surface heteroatoms, especially oxygen groups, affects the electrochemical response of the carbon materials in two different ways. First, the oxygen groups may determine the wettability by the electrolyte solution. The increase in oxygen content varies the electrostatic field in the surface, imparting certain polarity, which makes easier the interaction with water molecules [12]. In addition, the surface oxygen groups may experience redox reactions that might present a significant contribution to different processes [12].

In this way, some works in the literature have discussed the chemical change on diamond film surface and its relation with the hidrophobicity/contact angle has been made by different surface treatments (hydrogenation and oxidation) [2,3,7]. By continuing this subject investigation, this work presents the change of the chemical surface oxidation of NCD by increasing the methane

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concentration in gas mixture during the film growth. The evolution of oxygen content on such films was analyzed by X-ray photoelectron spectroscopy (XPS) and contact angle measurements. In particular, a detailed description of the nature and the relative abundance of the dominant chemical species were obtained. Consequently, the discussion and results were mainly focused on the correlation between the observed quantitative and qualitative changes on the surface composition.

2. Experimental

Depositions were performed using hot filament chemical vapor deposition (HFCVD) technique with substrate temperature around 1020 K, pressure inside the reactor of 4.0 kPa and deposition time of 10 h. The CH_4 concentration varied from 0.5 to 2.0 vol.% in gas mixture of Ar/H_2. The Ar concentration was kept in 90 vol.% during all experiments. These values were chosen from our previous work, where among different NCD films obtained from different Ar and CH_4 concentrations, the best one was grown with 90 vol.% [13,14]. The process of nanodiamond growth was terminated in H-atmosphere during all the cooling down stage that was around 10 min. The films were grown on polished silicon (1 0 0) 1 cm × 1 cm prepared by ultrasonic hexane bath with 0.25 μm diamond powder during 60 min. Films morphology and roughness were evaluated by a Nanoscope V Multimode atomic force microscope (AFM) in air. The AFM was operated in tapping mode with a scanning rate of 0.2 Hz for all scanning sizes using an etched silicon probe (k = 50 N/m). The root mean square roughness (R_{rms}) was observed from the surface topography of AFM images. The film's quality and stress was evaluated by micro-Raman scattering spectroscopy (Renishaw microscope system 2000) using the 514.5-nm line of an argon ion laser taking the spectra covering the range from 800 to 2000 cm^{-1}. The collected spectra were fitted after baseline subtraction using five Gaussians curves at 1150, 1332, 1345, 1490 and 1560 cm^{-1}, which demonstrated the suitable curve shape.

Table 1
Dipole moment, surface tension and its components for wettability test liquids.

Liquid	Dipole moment (D)	γ (mJ/m^2)	γ^A (mJ/m^2)	(^{p} (mJ/m^2)
Water	1.84	72.8	21.8	51.0
Di-iodomethane	1.13	50.8	48.5	2.3

XPS experiments were performed at the Brazilian Synchrotron Radiation Laboratory (LNLS) using the bending magnet beam line with a Double Crystal Monochromator (SXS). It was recorded the C1s, O1s, using InSb crystal (1 1 1) at 1840 eV at a fixed pass energy of 23.5 eV for the short scan and 58.7 eV for the long scan Survey spectra and at pressure of 2.2×10^{-8} mbar. Binding energy values were calibrated with respect to the $Ag3d_{5/2}$ signal and $Au4f_{7/2}$. Sessile-drop contact angle measurements and surface energy results were carried out on a Krüss Easy Drop system by calculating the contact angle (θ) between the diamond layer and liquid drop with test liquids (listed in Table 1, together with surface tension components and dipole moment) [15–18] at room temperature and atmospheric pressure. The measurement of the contact angle was always performed immediately after the drop placement on the surface, in order to avoid the measurement which is perturbed by the evaporation process, with accuracy ±3°.

3. Results and discussion

Low magnification AFM images over a 14 μm ×14 μm area permitted a detailed observation of the NCD films roughness and grains morphology correlated with their clusters formation as a function of the CH_4 increase in the feed gas, between 0.5 and 2.0 vol.%, as shown in Fig. 1(a)–(d). The samples morphology is characteristics to those of CVD ballas diamond, showing contin-

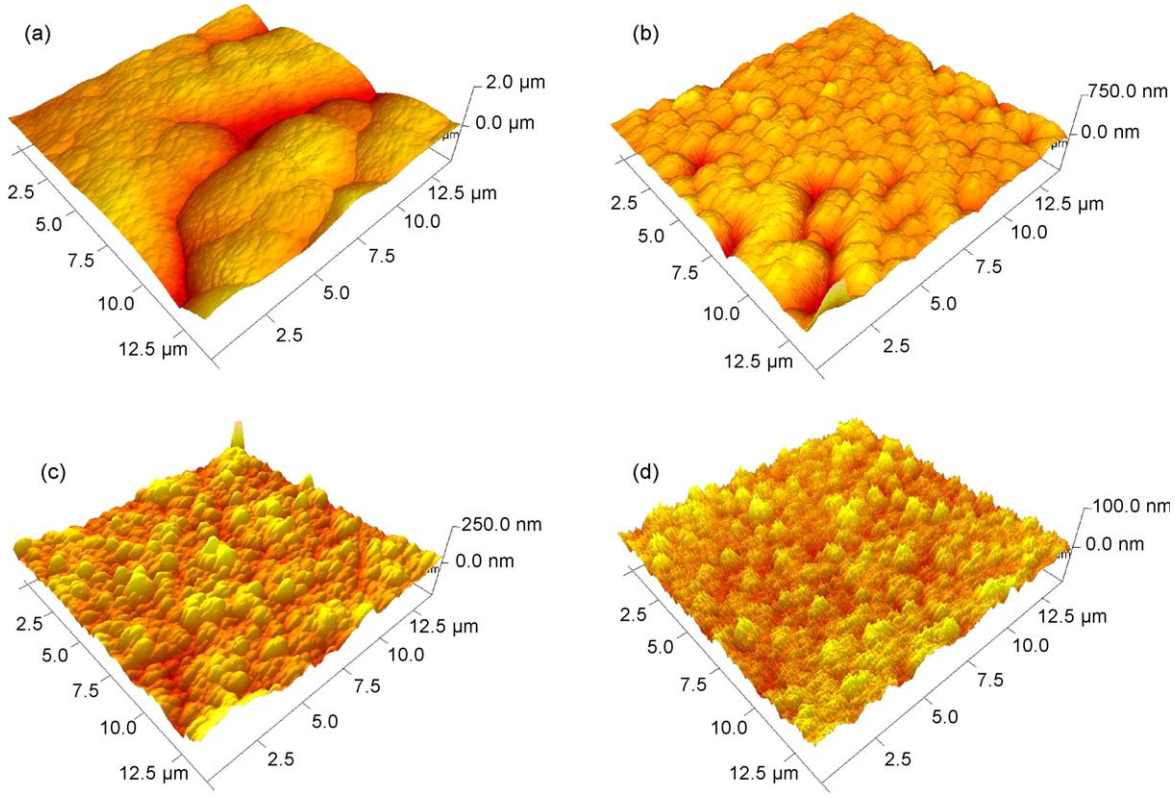

Fig. 1. AFM topographic images of NCD films grown on Si substrates with (a) 0.5%, (b) 1.0%, (c) 1.5% and (d) 2.0% of CH_4 in gas mixture, respectively.