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Nanostructured diamond-like carbon films characterization

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ABSTRACT

In this work, we have studied the influence of the substrate surface condition on the roughness and the structure of the nanostructured DLC films deposited by high-density plasma chemical vapor deposition. Four methods were used to modify the silicon wafers surface before starting the deposition processes of the nanostructured DLC films: micro-diamond powder dispersion, micro-graphite powder dispersion, and roughness generation by wet chemical etching and roughness generation by plasma etching. The reference wafer was only submitted to a chemical cleaning. It was possible to see that the final roughness and the sp^3 hybridization degree (that is related with the structure and chemical composition) strongly depend on the substrate surface conditions. The surface roughness was observed by AFM and SEM and the hybridization degree of the DLC films was analyzed by Raman Spectroscopy. Thus, the effects of the substrate surface on the DLC film structure were confirmed. These phenomena can be explained by the fact that the locally higher surface energy and the sharp edges may induce local defects promoting the nanostructured characteristics in the DLC films.

1. Introduction

One of the many forms of carbon, diamond-like carbon (DLC) or tetrahedral amorphous carbon (ta-C), consists mainly of sp^3 bonded carbon atoms. However, the DLC does not have a unique composition, but consists of a mixture of amorphous and crystalline phases [1–3]. DLC films contain carbon atoms in a variety of different coordinations. There are tetragonal coordinated sp^3 carbon atoms present in pure diamond as well as trigonal sp^2 coordination found in graphite, and possibly some sp^1-coordinated atoms. DLC films may contain microcrystalline diamond and graphite as well as a disordered structure containing a mixture of configurations. The physical properties of these films depend on the method of preparation. For a given method, the ratio of sp^3 to sp^2-coordinated carbon can be affected by the presence of hydrogen in the films [1]. The beneficial properties of DLC stem from the continuous rigid random networks of sp^3 carbon atoms, and the properties can essentially be tailored by controlling the sp^3/sp^2 ratio [4–7]. The deposition mechanisms of DLC can be described in both macroscopic and microscopic terms. The macroscopic view attributes the formation of DLC to a phase transition between sp^2 (a-C) and denser, metastable sp^3 bonded DLC. The microscopic view describes the ion processes giving rise to sp^3 bonding. Many deposition mechanisms of DLC films have been proposed, but very difficult to show an exact model for growing DLC films, because several parameters can influence in the deposition mechanisms of DLC films (deposition techniques, time, precursor, DC BIAS applied powers, etc.) [8–16]. Using the HDPCVD for the deposition of nanostructured DLC film, the deposition mechanism is not influenced by sub-plantation or by preferential sputtering of the sp^2 and sp^3 sites, because in a HDPCVD system there is no DC bias applied to the samples. In this case, the main mechanism for obtaining nanostructured DLC films occurs changing the surface energy. The surface energy is increased when different substrate topographies and different kinds of micro- and nano-powders on the surface substrate (diamond and graphite powder) are used. In this work, nanostructured DLC films were obtained with low surface roughness and high sp^3/sp^2 hybridization ratio [17,18]. The different substrate surface preparations have strong influence on the characteristics of the nanostructured DLC films, as is shown in this work.

2. Experimental

The nanostructured DLC films were produced in an HDPCVD system that uses a new concept of plasma generation. In this case, a planar coil coupled to an RF system for plasma generation, and an electrostatic shield for plasma densification are used, in this mode high-density plasmas are obtained. For the ion acceleration another RF system in planar configuration is used as seen in Fig. 1. The substrate temperature was not controlled, but measured by a type K thermocouple, which indicated that the temperature never exceeded 90 °C. For the deposition of the films, pure methane plasma processes were used. The substrates used to deposit the films were three-inch diameter silicon wafers, 380 μm thick and orientation (1 0 0). They were submitted to a Piranha clean, followed by a diluted HF dip, before the modification of the surface. The surface modification is important for the increase of the surface

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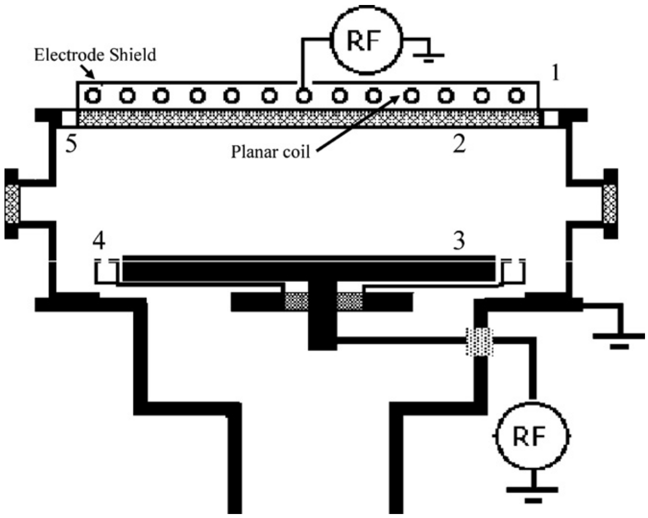

Fig. 1. Scheme of the high-density plasma chemical vapor deposition system. (1) Planar coil with an electrode shield, (2) pyrex window, (3) electrode, (4) secondary distributor of gases and (5) main distributor of gases.

energy of the silicon wafers. Four methods were used for the surface modification of the samples: diamond powder (<1 μm) dispersion (deposition by spinner, 1000 rpm, 30 s); graphite powder (<5 μm) dispersion (deposition by spinner, 1000 rpm, 30 s); roughness generated by plasma etching (RIE system, SF_6 plasma, 6.67 Pa, 100 W, 2 min); roughness generated by wet chemical etching (one part of fluoridric acid and nine parts of nitric acid or TMAH (2.5%wt @ 80 °C) solution and the reference substrate was only submitted to a chemical cleaning). For each method, the DLC films were deposited with four different deposition times: 1, 2, 3 and 4 h. After preparation of the samples, the DLC films were deposited. The parameters of the DLC films depositions were: 2.00 Pa, 250 W (coil power, RF, 13.56 MHz, remote plasma), 40-sccm methane. In these conditions, the deposition rate was 47 ± 1 nm/min. The deposition rate is independent of the surface topography, and is directly related to the process conditions. For evaluating the deposition rate, we measured the DLC thickness, using a Dektak 3030 perfilometry from Sloan-Vecco. For the analyses of the nanostructured DLC films, we used an AFM microscope model SPM 9500J3 (Shimadzu). Each sample was analyzed in the AFM in the tapping mode. For each sample, we have made 10 analyses: 5 analyses in different areas of 15 μm × 15 μm and 5 analyzes in different areas of 5 μm × 5 μm. The scanning electronic microscope used for analyzing the DLC films was a FEI NOVAnano400 microscope. We analyzed the surface topography of the samples and the lateral profile after the final deposition. We analyzed the nanostructured DLC films with a vis–UV Raman Spectroscopy system. The spectra were collected using a Renishaw micro-Raman 2000 spectrometer on a 40× objective with a photo multiplicator. Unpolarized Raman spectra were acquired at $\lambda = 514.5$ nm, the spectral resolution was about 4–6 cm^{-1} and the power on the sample was kept well below 1 mW. For calculating the intensities and the areas of the peaks in the Raman spectra, we have made the deconvolution of these spectra (with Gaussian fit), using the Microcal Origin program, with Peak Fitting Mode. The results obtained are shown in this work.

3. Results and discussion

High-density plasma is quite for the growth of good quality nanostructured DLC films. But the properties of these films are largely dependent on the deposition conditions. The roughness of the nanostructured DLC films is important, in this situation, because it is affected by surface topography. Fig. 2 shows the R_{ms} roughness of the nanostructured DLC films deposited by the HDPCVD system as a function of the deposition time. The R_{ms} roughness was analyzed in two different sizes in each sample (5 μm × 5 μm and 15 μm × 15 μm) and we made five analyses per size. The measurements were made in this way to check if the DLC roughness does not change when the analyzed area changes, checking the data reproducibility. With the AFM analyses we checked if roughness does not change with the analyzed area for the nanostructured DLC films, and the standard deviation was less than 1%. Observing Fig. 2, we could see that roughness depends strongly on the surface topography of the samples and on the final deposition time.

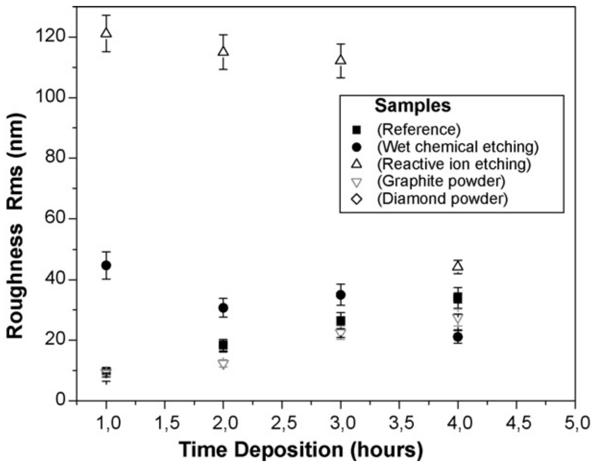

Fig. 2. R_{ms} Roughness as a function of the process parameters.

For the nanostructured DLC films deposited by HDPCVD, just as for the deposition of others kinds of carbon films, the growth mechanisms for obtaining these films are not totally known. In this work, we used different surface topographies for obtaining different kinds of nanostructured DLC films. In this situation the roughness depends on the surface topography. Films deposited on the reference samples and on the samples with diamond and graphite powder, showed less roughness than the DLC films deposited on the etched surface (plasma etching or wet chemical etching). For the DLC films deposited on the samples with powders, the roughness increases with the deposition time, and for the films deposited on the etched samples, the roughness decreases with the deposition time. The roughness for the plasma etched samples before the depositions were approximately 150 nm and for the wet chemical etched samples were approximately 55 nm. In Fig. 3, we compared atomic force microscope (AFM) images from nanostructured DLC films deposited by the HDPCVD system. And in Fig. 4, we compared SEM micrographics from these films. These images are from samples with a deposition time of 4 h. The surface morphologies of DLC films are very different from each other, and all samples have different grain size. The different grain sizes are dependent on the surface topography before the film deposition. Larger grain size can produce more roughness. Different surface topographies lead to a different DLC film growth. For example, for the DLC films deposited on rough surfaces (plasma etching), at first, the atoms are accumulated in the holes that are existent on the surface substrate, but they cannot fill all the holes on the surface, in this situation the roughness is larger for smaller deposition time (for the deposition time of 1 h, the roughness was 120 nm). When the final time is increased, the atoms fill the holes and are accumulated around the islands (formed by the filled holes) and the roughness decreases. This effect promotes the reduction of the surface energy. This effect is related to the DLC films growth rates. A smaller surface energy on the substrate is related to a smoothing effect in the films deposition, and in this condition, the roughness is smaller, because the atoms have more easiness to form the DLC films. If the surface energy is high, the roughness increases, because the atoms need the high energy to be leagued and to form the film. In this situation, the final roughness of the DLC films is strongly related to the surface energy [19,20].

For longer deposition time, the atoms cover every island and the spaces between one island and another, forming a continuous film (for the deposition time of 4 h, the roughness was 40 nm). The same effect occurs with the films deposited on the sample etched with chemical wet. For the DLC films deposited on the surface with diamond and graphite powder, the roughness increases with

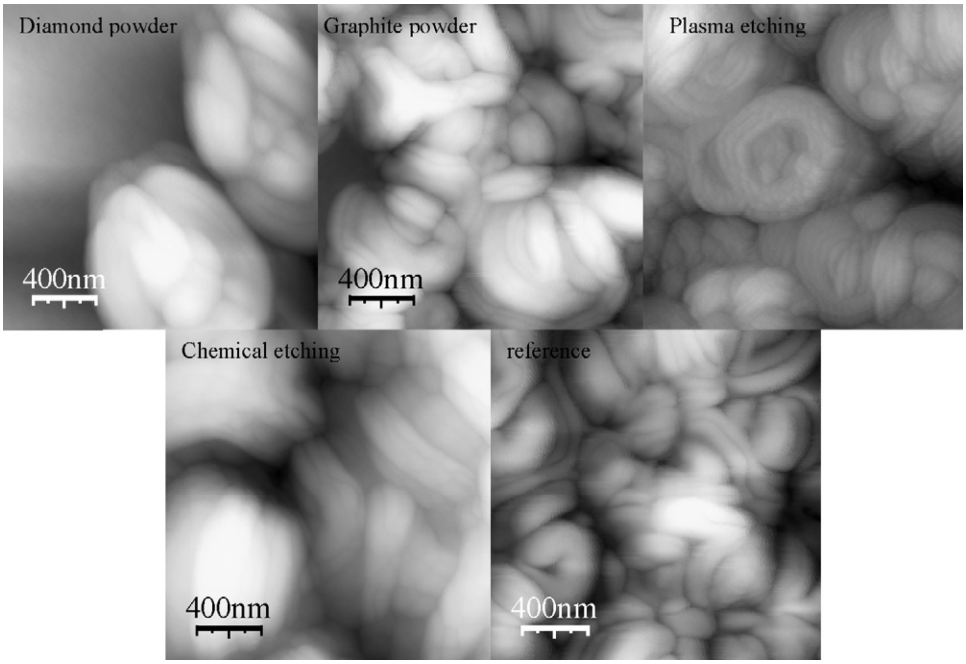

Fig. 3. AFM images of nanostructured DLC films, with final time deposition of 4 h: (1) with diamond powder, (2) with graphite powder, (3) with plasma etching, (4) with wet chemical etching and (5) reference sample.

the deposition time. For these processes, the initial surface energy increases with the deposition time, and the roughness increases too. These effects occur because of the influence of the surface topography substrate before the nanostructured DLC films deposition [21,22].

We have noticed that the DLC films deposited in reference sample by the HDPCVD system, showed the D and G bands well-defined in the Raman spectra and the central position of these bands is around 1330 and 1540 cm^{-1}, respectively. For these samples, when the deposition time increases, the increasing of the I_D/I_G ratio occurs. The increasing of the I_D/I_G ratio is related to the increasing of the sp^3 bonds in the DLC films. This effect can be confirmed with the presence of a small peak around 950–1000 cm^{-1}, this is related to the formation of sp^3 bonds due to the presence of C–C sp^3 bonds related to the tetrahedral structures in the DLC films. For the reference samples the high density used for depositing the films, promotes high energy during the growth films that increases sp^3 bonds in these films.

Due to the presence of other kinds of structures formed in the DLC films, the modification of the surface topography substrates before the deposition process. We observed that the D and G bands appeared at around 1270 and 1500 cm^{-1}, respectively. For the films deposited by the HDPCVD system on surfaces with diamond and graphite powder, and etched by chemical wet and plasma, the Raman spectra showed the first-order G band (around 1500–1600 cm^{-1}) and D band (around 1230–1340 cm^{-1}), and some

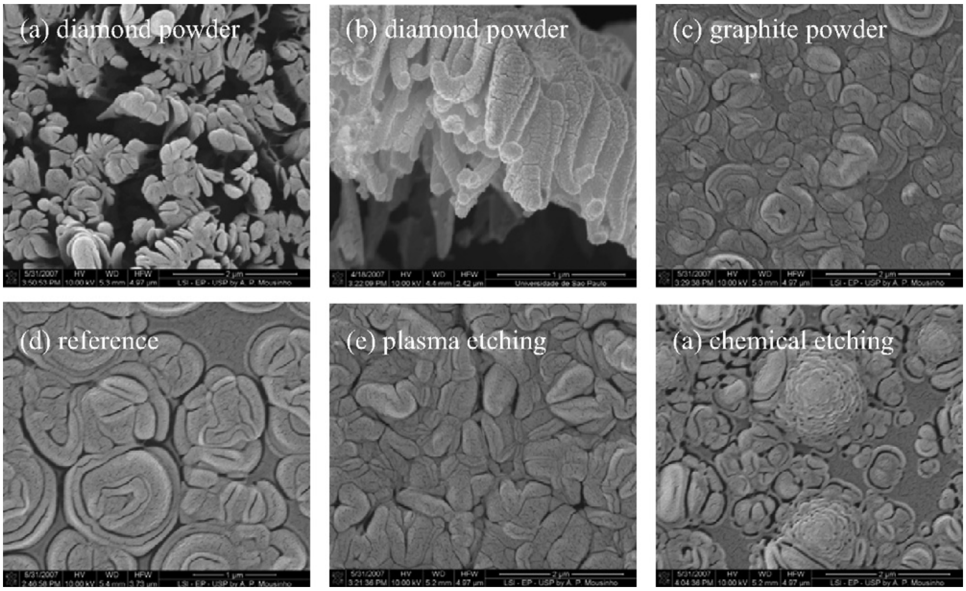

Fig. 4. SEM micrographs of nanostructured DLC films, with final time deposition of 4 h (with 40,000×): (a) and (b) with diamond powder; (c) with graphite powder, (d) reference, (e) with plasma etching and (f) with wet etching.

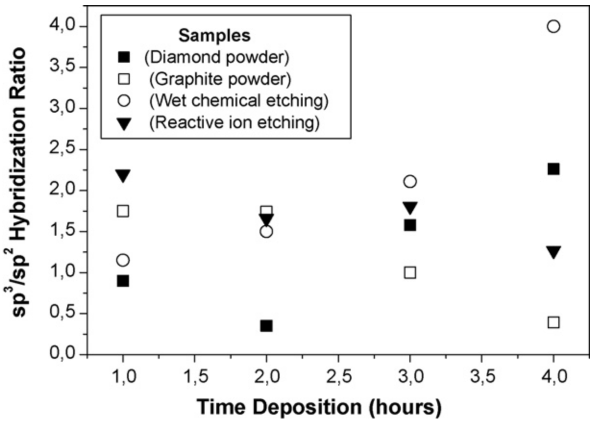

Fig. 5. I_D/I_G ratio as a function of the process parameters.

second-order peaks (combination bands at approximately 1000, 1750 and 1860–925 cm^{-1}). The second-order bands are related to the presence of the nanostructures in these films (tetrahedral structure formation with high sp^3 bonds concentration) and the formation of carbon nanotubes during the growth deposition [23]. The intensity for all bands in the Raman spectra depends on the surface topography substrate and on the deposition time.

First, we analyzed the D and G bands of the DLC films deposited by the HDPCVD system. Fig. 5 shows the I_D/I_G ratio as a function of the deposition time. We noticed that I_D/I_G ratio is strongly dependent on the deposition time and of the surface topography used. For the films deposited on the reference sample, diamond powder and wet chemical etching, the I_D/I_G ratio increases when the deposition time is increased. For the films deposited on a surface with graphite powder and plasma etching, the I_D/I_G ratio, decreases when the final time deposition is increased. These effects are related to the second-order bands due to the presence of nanostructures in the films and the surface energy generated by the different surface topography used. For the films deposited on the surface etched with plasma, the initial surface shows high roughness (approximately 150 nm). In this situation, the initial surface has structures with high aspect ratio (characteristic of the plasma etching processes).

The structure formed due the plasma etching are thin and the distance between one and the other is small. In this case, the surface energy is bigger, due to the presence of the privileged points of deposition and this promotes the sp^2 bonds formation, that increase with the deposition time, generating DLC films with graphite-like characteristics. With the use of graphite powder, we noticed a similar effect, but in this situation, the increasing of sp^2 bonds in the films, were promoted by the presence of graphite powder on the substrate surface. One of the characteristics of the graphite grains is the formation of bi-dimensional structures that privileged sp^2 bonds. This effect is stronger when the deposition time is increased, promoting the I_D/I_G ratio decreasing.

The presence of diamond powder on a substrate surface promotes the formation of tri-dimensional bonds (sp^3). Diamond powder is commonly used as seed for growing diamond films. For the DLC films deposited by the HDPCVD system, the powder promotes the increasing of the I_D/I_G ratio that is related to the sp^3 content. This effect increases when the deposition time is increased. For the films deposited on a surface etched with wet chemical, the I_D/I_G increased with the increasing of deposition time. The roughness generated with the wet chemical etching is smaller (compared with the plasma chemical etching), and in this case, the surface of the substrate before the deposition films is flatter. This effect promotes to the decreasing of the surface energy, contributing to the formation of clusters of sp^3 bonds.

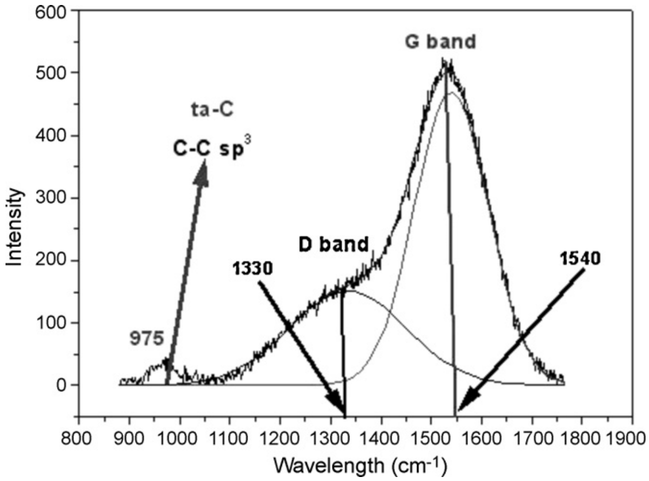

Fig. 6. Typical Raman spectrum for nanostructured DLC films deposited with pure methane plasma by HDPCVD system.

DLC films deposited on substrates with diamond powder show complex structures in the film composition; in this case the films have high disorder, which can be observed with the increasing of the D band. The use of diamond powder promotes the tetrahedral carbon bonds, with the high content of sp^3 bonds that can be confirmed with the second-order band around 1000 cm^{-1}. The final structure in nanostructured DLC films deposited with diamond powder is composed of amorphous carbon with graphite clusters, tetrahedral carbon (with high sp^3 content) and carbon nanotubes (around 1800–1970 cm^{-1} region).

With the DLC films obtained on surface etched by chemical wet, the I_D/I_G ratio increases with the deposition time (see Fig. 6), and the disorder increases too. In these samples, the formation of tetrahedral carbon structures in the films have occurred, but the carbon nanotubes formation has not. The intensity of the second-order band related to sp^3 bonds, increase with the deposition time. These effects are related to the flat surface generated when the samples are submitted to a wet chemical etching.

The DLC films deposited on surfaces with graphite powder showed minor I_D/I_G ratio, due to the long chains formation of graphitic structures with some tetrahedral carbon bonds clusters in the graphitic matrix, but these effects are decreased when the deposition time increases. In DLC films deposited on surfaces etched with plasma the I_D/I_G ratio decreases with the deposition time. The second-order band related to the tetrahedral bonds are formed but with low intensity. The different nanostructures formation for these films decrease when the deposition time increases and are related to the initial high roughness of the substrates.

4. Conclusions

In this work, it was studied the influence of the surface substrate topography in the formation of nanostructured DLC films deposited by the HDPCVD system. We have observed that the structure formation of these films depends strongly on the substrate characteristics. For different surface topography used in this work (diamond and graphite powder, plasma etching and wet chemical etching), the surface energy is changed, which influences the roughness and the structure formation of these films (graphitic, tetrahedral, carbon nanotubes, etc). For example, in the DLC films deposited using diamond powder, tetrahedral carbon formation has occurred (with high sp^3 content) in amorphous carbon matrix, and carbon nanotubes. The formation of these structures depends on the deposition time. On the other hand, this effect has not occurred in the DLC films deposited on a surface with graphite powder, where the DLC showed only bi-dimensional graphitic structure formations. This way, it was possible to confirm the effects of the surface energy in the results of the DLC films structure formation.

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