GROWTH PARAMETERS OPTIMIZATION TO SYNTHESIZE CVD DIAMOND THROUGH GRAPHITE ETCHING

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ABSTRACT

Diamond films were deposited from graphite etching as a carbon source with atomic hydrogen instead of using conventional hydrocarbon in the feed gas. A graphite plate was used as sample support in a hot filament chemical vapour deposition reactor. Graphite temperature, gas flow rate as well as the pressure inside the reactor presented a strong influence on the diamond growth rate, morphology and quality. Scanning electron microscopy images showed that the films grown at 600 and 700 °C depicted similar morphologies while the film grain size decreased as a function of the pressure and the gas flux increases. Raman analyses confirmed good diamond quality in the whole ranges of such parameters variation and was also used to analyse the sp^2/sp^3 ratios of the three produced sample sets. For deposition time of 4 h the process efficiency was evaluated from the ratio between the diamond mass after deposition and the mass lost by the graphite target. In the range of the experimental parameters studied the highest efficiency value was 0.43 obtained at 700 °C, for a pressure of 30 Torr and flux of 100 sccm, respectively.

1. INTRODUCTION

Among the many efforts made to improve diamond growth in large areas, hot filament chemical vapor deposition (HFCVD) growth process, without hydrocarbon in the feed gas, appears as a good alternative to reduce the cost besides promoting a higher growth rate compared to the conventional systems. Shin et al. [1] have discussed that high hydrocarbon concentrations may be a limiting factor in the diamond growth rate because they lead to graphite coating on the filament. This effect enhances the production of degraded diamonds with cauliflower-shaped or ball-like structure. An alternative way for obtaining diamond films with high growth rate and quality would be a high carbon content around the substrate but sufficiently low around the filament to avoid its graphite coating.

There are some authors in the literature that have already produced diamond without using hydrocarbon in the gas inlet. Chow et al. [2] have demonstrated that the chemical reaction products in the atomic hydrogen-graphite reaction may be used as an efficient starting material for diamond growth. Yang et al. [3] have found high growth rate of high quality diamond through graphite etching using different setups for graphite and substrate inside the reactor. Woo et al. [4] have also successfully investigated the diamond growth on various substrates from a solid carbon source. These authors have observed that different contributions are limiting factors for diamond growth and nucleation rates, such as distance between filament and substrate, the position of graphite plate and definitely the strong influence of the graphite temperature.

Likewise, the growth parameters influence showed to be an important study to synthesize CVD diamond films using a solid carbon source. For example, the pressure parameter was already studied by Kim et al. [5] when hydrocarbons are used in the CVD process. This work discussed the nucleation density dependence with pressure associated with the competition between the SiC layer formation and the atomic hydrogen etching, which decreased the nucleation sites. In similar way, Scwarz et al [6] have observed high growth rates for films grown with pressure lower than 20 Torr. This behavior was associated with the higher mean free path of the reactive species leading to the lower radical recombination. Similarly, some papers also presented the flux variation for values higher than the standard 100 sccm as a tool to improve diamond nucleation rate and growth on carbon substrates [7,8].

Taking into account the temperature variation, in our previous work we discussed that the graphite temperature demonstrated to have a strong dependence with the diamond nucleation for films grown during 15, 30 and 60 min [9]. Higher nucleation rates at lower graphite temperatures of 600 and 700 °C was observed and an accentuated nucleation decrease was observed at 800 and 900 °C where the diamond grains almost disappear, showing only few and small regions with grains at the sample border. In this article, we continue this study of diamond growth on silicon substrate from graphite as a carbon source using a setup similar to that of the experiments of Shin et al [1]. In this configuration the substrate is kept on graphite plate mounted in the support with a well controlled heating system to ensure a uniform temperature distribution on the whole graphite surface during the experiments. Thus, the goal of this work is to present, in a systematic way, the influence of: a) the graphite temperature between 600 to 900 °C, b) the pressure variation between 20 and 50 Torr and c) a flow rate variation from 100 to 500 sccm, using three sample sets for diamond films grown during 4 h. So, the optimized parameters associated with the diamond film morphology and quality are presented, using this growth configuration. Moreover,

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the process efficiency was calculated from the ratio between the diamond mass after deposition and the mass lost by the graphite target.

2. EXPERIMENTAL

Diamond films were grown in the hot filament chemical vapor deposition (HFCVD) reactor. Polished p type Si (100) substrates were ultrasonically treated in a solution of 0.25 um diamond powder dissolved in hexane during 1 h followed by their cleaning in acetone for 15 min. Sample support was mounted for keeping the graphite and silicon sample about 3 mm below three tungsten filament of 123 µm diameter. The filament temperature was 2100 °C, measured by an optical pyrometer. Si samples were cut 5 mm x 5 mm in size and they were kept over a graphite plate of 35 mm x 35 mm with 5 mm thickness. The whole sample area is covered by the filaments and the graphite plate area is much greater than Si samples. Graphite plate temperature was measured by a k type thermocouple situated in its central region from a small hole. So, the assumption that they are in thermal equilibrium is completely coherent. To clarify this explanation a schematic diagram of the sample support was already present in previous work [9] evidencing the thermocouple position inside the graphite plate. All sample sets were grown during 4 h. For the sample set concerning the temperature variation, the growth parameters were hydrogen flux of 100 sccm for a deposition pressure of 20 Torr at four different temperatures of 600, 700 800 and 900 °C. For the sample set with pressure variation from 20 to 50 Torr, the chosen growth temperature and flow rate were 600 °C and 100 sccm, respectively. Whereas for the sample set produced in the flow rate range from 100 to 500 sccm, the pressure and temperature were kept at 20 Torr and 600 °C, respectively. The graphite plate was polished with a silicon carbide paper 1200 grid before each experiment to ensure similar graphite surface for all experiments. For each experiment one specific graphite target was used and its mass was measured before and after the respective film growth. Diamond samples morphologies were studied from images obtained by JSM310 Jeol equipment. A Renishaw 514.5 nm Raman system was used for diamond films spectra.

3. RESULTS AND DISCUSSION

To optimize the experimental parameters and to find the influence of the substrate temperature, the pressure inside the CVD reactor and the total gas flow rate on the diamond films properties, three sample sets were studied as described in the experimental session. As already mentioned the efficiency of the hydrogen graphite etching strongly depends on its temperature and was discussed that at 600 °C this etching presents a maximum efficiency [10]. Speaking of that, the fist sample set analyzed was the diamond films grown as a function of the graphite temperatures of 600, 700, 800 and 900 °C. In the sample support configuration used in this work the thermocouple just indicates the temperature at graphite region that is etching by the atomic hydrogen, which also may represent the Si substrate temperature. Different film morphologies were observed by scanning electron microscopy (SEM) images and confirmed our already published results for the film nucleation rate in similar conditions and at different growth times [9]. It was observed the higher nucleation rates at lower graphite temperatures of 600 and 700 °C for growth time of 15 min. For samples grown at 600, 700 and 800 °C during 4 h the films are well faceted with predominant (111) orientation and grain sizes between 1 and 2 μ m. For films grown at 900 °C there is not a closed film layer, but only agglomerates with small faceted grains lower than 1 μ m. By comparing, Fig. 1 (a) and (b) show the SEM images for films grown at 600 and 900 °C, respectively.

From these results and our previous study [9] the second sample set were prepared observing the pressure influence on diamond morphology and quality. The flow rate was 100 sccm for a graphite temperature at 600 °C. Fig. 1 (c) and 1(d) shows the SEM images for films grown with 30 and 50 Torr. In the pressure range studied, between 20 and 50 Torr, the tendency observed was a film grain size decrease as function of pressure increase, associated to the decrease in the film growth rate. The film grown of 20 Torr presented grains of almost 2 µm while the film grown at 50 Torr presented grains of around 1 µm. The pressure effect is to promote a larger radicals mean free path in the gas phase as the pressure values become lower. This behavior contributes to the etching rate increase of the free radicals on the substrate surface permitting a larger number of radicals available for the film growth. As a rule, the etching by atomic hydrogen is enhanced at lower pressures because the amount of atomic hydrogen reaching the substrate increases as the pressure decreases due to the increase of the mean free path. Fig. 1 (c) and 1(d) may also be compared with film presented in Fig 1(a) of 20 Torr.

The last sample set analyzed concerns about the diamond film grown as a function of the gas flow rate were the pressure chosen was 30 Torr for the graphite temperature at 600 °C. In the flow rate range studied, between 100 and 500 sccm, similar tendency of the film grain size decrease as the flow rate increased was observed and is also associated with the mean free path decreased. For films grown with 100, 200 and 300 sccm the morphologies are very similar and substrate surface was completely covered while for films grown with 400 and 500 sccm only large agglomerates where observed and some unfilled spaces (not shown). For a better observation of such morphologies, the Fig. 1(e) and 1 (f) depict the SEM images for films formed with 200 and 500 sccm, respectively, and also may be compared with film presented in Fig 1(c) with 100 sccm.

A sequential and systematic Raman analysis was also made for the three sample sets studied and permitted to evaluate the diamond content in each set as a function of the three varied growth parameters. This behavior evolution is associated with the previous discussion of the morphology images. Using a Renishaw microscopic system 2000, micro-Raman spectra were recorded in backscattering configuration at room temperature employing the argon-ion laser excitation line (514.5 nm). The laser beam was focused on the sample using the objective with magnifications of 50x that correspond to the spot size of $\sim 2.0 \ \mu\text{m}$ in diameter for a beam penetration depth estimated in approximately 5.0 μm .



Figure 1 - SEM images of CVD films grown at different experimental parameters. (a) and (b) represent the films grown at 600 and 900 °C, respectively, hydrogen flux of 100 sccm and pressure of 20 Torr. (c) and (d) show the films grown at 30 and 50 Torr, respectively, hydrogen flux of 100 sccm and temperature of the 600 °C. Finally, images (e) and f) depict the films grown with hydrogen flux of 200 and 500 sccm, respectively, pressure of 30 Torr and temperature of the 600 °C.

The relative amount of diamond, also called diamond purity, might be obtained by a quantitative analysis of the Raman spectrum. To separate the contributions of diamond and disordered graphitic phases to the total Raman scattering, the whole Raman spectrum was fitted with Lorentzian lines, subtracting the background contribution due to the luminescence effect. To fit the broad band centered at 1550 cm⁻¹, it was necessary to take three different contribution bands: the D and G peak of polycrystalline graphite at around 1345 and 1560 cm⁻¹, and a low intensity band centered approximately at 1470 cm⁻¹ attributed to a tetrahedrally bonded diamond precursor. The amount of diamond in the films can be calculated by a relative Raman cross section of diamond to graphite of 1/50 by the relation [11]:

$$C_{d} = 100A_{d} / (A_{d} + \frac{\sum A_{i}}{50})$$
(1)

where A_d and A_i are the areas of the fitted curves corresponding to the 1332 cm⁻¹ diamond peak and the graphitic bands, respectively. This procedure was accomplished for all grown diamond films.

The results of diamond content are presented in Fig. 2 for the three sample sets and confirmed the high quality of such films that presented diamond purity between 97 and 99 %. Also, these results establish the good effectiveness of this methodology to grow diamond from a solid carbon source in the whole range of experimental parameters presented in this discussion. Even taking into account this small variation, some specific parameters justify pointing out the higher C_d values. Although a small variation took place, a brief observation of Fig. 2 shows a set of parameters where the best quality films were produced at 600 and 700 °C, for a pressure of 30 Torr, and from 100 to 300 sccm. So, we can produce high quality diamond films using lower temperature than those usually used when the carbon source is from hydrocarbon in the feed gas.



Figure 2 - Amount of diamond relative to sp² phase (diamond purity) as a function of substrate temperate, pressure and gas flow rate.

For all the things considered, the process efficiency to etch the graphite by the hydrogen for the diamond formation (EP) was evaluated for each sample. This efficiency is obtained from the ratio between the diamond mass on the substrate (m_s), after the deposition and the lost mass by the graphite (m_e) after the etching by the relation [4]:

$$EP(\%) = (m_s/m_g) \times 100$$
(2)

The Fig. 3 shows the EP values calculated as a function of the three parameters studied: graphite temperature, pressure inside the reactor, and gas flow rate. As may be observed the EP presented maximum values for growth temperature of 700 °C, pressure of 30 Torr, and flow rate of 100 sccm. The discussion of the results may be associated with two contributions: the graphite etching efficiency and the more suitable experimental conditions for diamond formation. Considering our results discussed in previous work [9] we have analyzed that all the graphite samples presented severe etching that caused a visible physical damage on the target. Significant difference on both morphologies, i.e., of graphite target etched at 600 and the same one etched at 900 °C were observed. However, preferential etching was not observed, as a function of the target temperature. For the sample etched at 900 °C, its morphology only presented deeper holes than that for graphite etched at 600 °C. This behavior was attributed to the original graphite surface which already has a high disordered level.



Figure 3 - Efficiency for the diamond formation (EP) as a function of substrate temperate, pressure and gas flow rate.

In addition, the dependence of graphite target temperature on this etching process has been analyzed considering the mechanism of atomic hydrogen transport in carbon materials. The dependence between the apparent diffusion coefficient and the target temperature was studied by some authors and presented a large discrepancy [12-14]. In spite of this discrepancy, in the range from 600 to 900 °C the diffusion coefficient showed at least a difference of two orders of magnitude. These studies enable us to infer that at 900 °C the hydrogen may penetrate deeper in the graphite enhancing a disordering region that generated a higher contribution to D band observed from Raman spectra at this target temperature as discussed in previous work [9]. With this in mind, we may infer that at higher temperatures of 800 and 900 °C occurred a supersaturating of carbon on the growth surface that inhibited the radical formations necessary to growth diamond leading to the lower EP values than that for 700 °C. On the other hand, for sample grown at 600 °C this lowest EP value is associated to its lowest substrate temperature to grow diamond promoting this lowest growth rate. Concerning the EP value behavior as a function of pressure and flow rate, the explanation may be also associated to the mean free path, already considered above. In spite of the fact that this relation is related to the film mass, it seems that such results may also be correlated to the diamond purity C_d from Raman spectra. The better diamond films are associated with the higher EP values. This behavior also corroborates with our previous discussion.

4. CONCLUSIONS

A series of experiments were made to optimize the methodology to grow diamond films using a target of solid carbon. Analyzing the EP and C_d, the best experimental parameters used in this growth process were graphite temperature of 700 °C, gas flow rate of 100 sccm and pressure of 30 Torr. These results are in good concordance with the highest diamond purity in such films. Besides, these film morphologies also showed the highest grain sizes related to their highest growth rate. This behavior may be attributed to the competition between the more appropriated temperature to grow CVD diamond and the etching of the graphite target. The association between EP values and diamond purity seems reasonable because the efficiency to etch the graphite target is directly related to the available atomic hydrogen on the growth surface that also is the main radical responsible to form high quality diamond films. Also, it is important to point out that the use of different solid carbon targets with different graphitization index could drastically change the experimental results. However, the presented results and discussion represent a very good guide to grow diamond using different solid carbon source.

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