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THE DIAMOND GROWTH – CVD ASSISTED BY HOT FILAMENT IN SILICON SUBSTRATE IN 80 cm^2 AREAS

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ABSTRACT

Nowadays, the diamond grown by chemical vapor deposition (CVD) is seen economically as one of the most interesting materials, due to its vast application, mainly in short-term, resulting from diamond's unique properties. Its applications reach many technological areas, standing out the mechanics area due to possibilities use as cutting tools, tribological layers in automobiles and aeronautical engines, heat sinks, surfaces protection for aggressive environments and abrasive special devices which also add applications in biological areas. The largest obstacle for these applications is the high cost of diamond films production if compared commercially with other alternative materials. So, the area and the growth rate increasing is a solution for the costs reduction in the diamond production. The CVD diamond samples used in this work had been grown in a big reactor, for growth in big areas, by the hot filament chemical vapor deposition technique (HFCVD). The precursory mixture of 2% of methane in hydrogen was maintained by a of 50 mbar pressure for a E2M8 - Boc Edwards vacuum pump. The substrate used in the growths was silicon (100) with 100mm of diameter. The growth temperature was maintained in (800 ± 20) °C and the growth time was changeable until about 50 h, when it had the breaks of the substrate. The diamond growth rate measured (0,7 ± 0,1) μm/h is low for economic viability of the process. The spectroscopy of Raman scattering analysis evidences the diamond growth of good quality, approximately in one area of 80 cm^2, with minimum compressive stress. The properties and the diamond growth rates the surfaces of the used substrate had been uniform. The reached development allows diamond growth 30μm thickness in 80 cm^2 areas, without breaking of the substrate.

1. INTRODUCTION

1.1 The diamond and its properties

The diamond possesses some of the most extreme physical properties, such as: bigger toughness (90 GPa), smaller compressibility (8,3.10^{-13} m^2.N^{-1}), bigger thermo conductivity in room temperature (2.10^3 W.m^{-1}K^{-1}), low expansion coefficient (1.10^{-6}K^{-1}). It is transparent in the spectral region from the ultraviolet to the infra-red, good electrical insulating in room temperature; it possesses attrition coefficient equivalent to Teflon, high index of refraction (2,417 for sodium yellow light λ = 589 nm); it admits various types of dopes chemically inert in room temperature, resistant to cosmic radiation and it attends requisites to bone implants [1,2].

The simple observation of some of these properties indicates that the diamond is insuperable for cutting and abrasion of non-ferrous materials. In fact, the use of natural diamond in cutting tools and abrasion has been already established. The industrial use of this type of tool has become a reality since the 50s in the XX century, with the artificial production by the high pressure and high temperature process (HPHT). However, the diamond practical use, in Science and Engineering, was limited for being scarce and expensive. It begins to exist the possibility of explorating these properties for many applications, revealing the diamond as a promising material of the Engineering materials, with the recent development of the techniques to grow diamond films, in a variety of support materials, or substrate.

In spite of reaching a big development and of the unambiguous advantages in the diamond applications, its use hasn't achieved the levels for the foreseen markets yet. As an Engineering material, the diamond still finds an obstacle for its dissemination and popularization: the high cost of diamond films production commercially compared with other alternative materials. The researchers' efforts in reducing these costs have been very big in the last years. With a cost of 50 to 100 dollars per carat, at the end of 80s in the last century, the last generation reactors can produce, nowadays, diamond with a cost of 5 dollars per carat [3].

In spite of the economical and scientific interest in promoting the growth of diamond in big areas, many references can't be found in the scientific literature about this theme. In fact, the diamond growth technology in big areas is surrounded by secrets.

The biggest interest in the development of the technology in the diamonds growth in big areas seems to be an answer to one of the limits in the diamond use as an Engineering material. The increasing of the deposition area and the growth rate is a solution for the cost reduction in the diamond production [4,5]. Promoting the growth in big areas, the diamond could be fractionated and it would allow its use with a low cost in the applications already established, mainly as cutting tools and abrasion of non-ferrous materials, beyond the possibilities of new applications, as in optical windows and heat sinks.

Basically, three methods to obtain the CVD diamond growth are promising for its production in big areas, two involving

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plasma and the other one, hot filament [6-9]. Among the methods, the one, which uses hot filament is superior due to its simplicity and facility in big areas. In this way, despite the plasma method present, growth rates of 10 μm/h till 50 μm/h, the consume of electricity and gases and the high initial cost of the equipment's made its use, in big areas of growth, cost relatively bigger. Thus, our intention is to go on studying the CVD diamond growth, using the technique assisted by hot filament.

2. EXPERIMENTAL DETAILS

The CVD diamond was grown in a big reactor, assisted by hot filament (HFCVD). The precursory mixture of 2% of methane in hydrogen was maintained at 50 mbar pressure by a E2M8- Boc Edwards vacuum pump. The substrate used in the growths was silicon with 100mm in diameter and 250 μm in thickness, polished with diamond paste 1μm. Figure 1 shows the used system scheme.

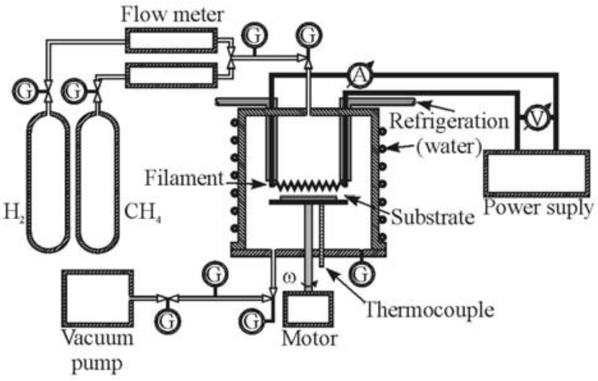

Figure 1 - Equipment assembly of schematized drawing.

The hydrogen (H_2) and methane (CH_4) gases are kept in different containers and mixed after the passage by two digital flow meter MKS 247 Type D. After the passage by the mixer, they are introduced in the reactor vacuum chamber, which is cooling by water in its external part. The vacuum chamber is connected to a vacuum pump that maintains stable pressure inward, propitiating one of the growth diamond conditions. An electric motor can rotate the substrate holder carrier at 0 to 0,1 Hz frequencies, in order to promote the temperature control over the substrate, aiming at the decreasing of the gradient temperature in the grown sample. The filaments are fed by a tension source AC at 220 V. A transformer can be used in order to pass direct and alternate currents through the filaments. In Figure 2, a schematized drawing is presented detailing the reactor inward, representing the substrate holder, the filaments holder, the windows of observation and the substrate rotor holder.

2.1. Study of the growth rate variation in function of the gaseous flow in the hfcvd big reactor

In order to obtain, experimentally, the optimum values of gaseous flows in the reactor, ten tests of diamond growth were done. In the first five tests, the gases inlet in the reactor was done by a "shower" which is composed by a pipe with a spiral shape, with holes of 1.0 mm of diameter turned to the sample, schematized in Figure 3a. In the other five attempts, it was used a simple pipe for the gaseous mixture inlet, schematized in Figure 3b. In all the tests, the following growth conditions were maintained: intensity of the total electric current in the filaments equal to 60,0 A, pressure in the reactor chamber equal to 50,0 mbar and the number of tungsten filaments, with 123 μm in diameter used equal to 15. The gaseous mixture flows were shown in Table 1.

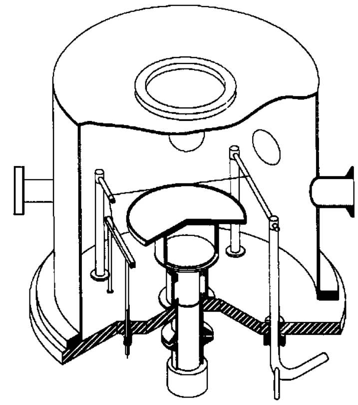

Figure 2 - Big reactor schematized drawing.

Table 1 - Growth conditions

Flow	Test				
(*sccm*)	1	2	3	4	5
H_2	100,0	200,0	300,0	450,0	600,0
CH_4	2,0	4,0	6,0	9,0	12,0

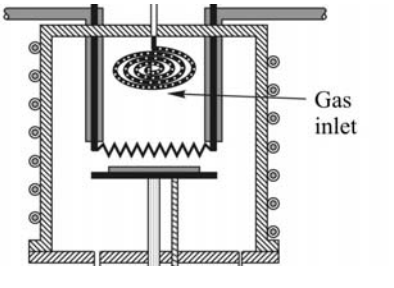

Figure 3a - HFCVD reactor with "shower" schematized drawing.

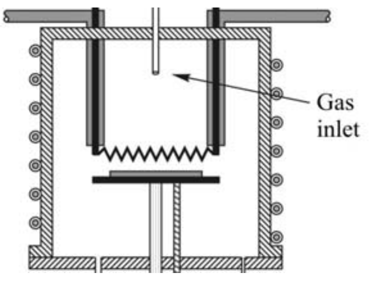

Figure 3b - HFCVD reactor with simple tube schematized drawing.

Besides the realization of the measurement in the growth velocity variation in function of the gaseous mass quantity in the reactor inlet, and its shape, analysis of Raman scattering spectroscopy (Renishaw 2000) and scanning electron microscopy (SEM JEOL JSM-5900LV) were done in order to verify the quality and the morphology of the grown diamond.

2.2. Establishing limits of the diamond growth in present developmental conditions

Samples were grown in order to establish the point one could arrive with the obtained development. Thus, two samples were grown in a relatively long time, with established ideas conditions in this work, until its destruction point.

3. RESULTS AND DISCUSSION

3.1. Study of the growth rate variation in function of the gaseous flow in big hfcvd reactor

The growth velocity varied in a non-linear shape in function of the gaseous mixture flow. In all growth cases, the proportion of 2% of methane was maintained.

Figure 4a shows the growth rates variation in function of hydrogen flow, using the “shower” as the gaseous mixture inlet.

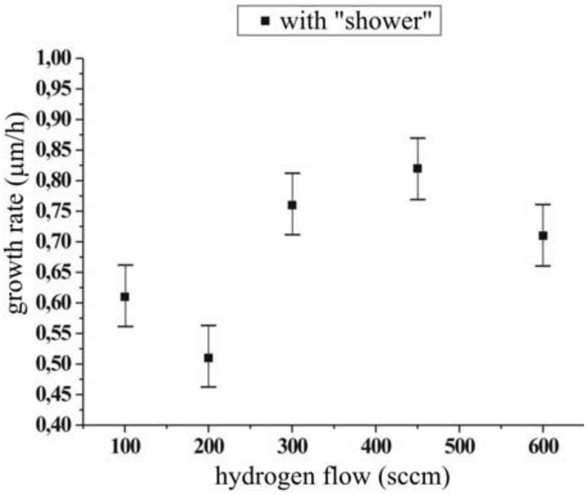

Figure 4a - Growth velocity (μm/h) X hydrogen flow (sccm), using the “shower” as the gaseous mixture inlet.

Figure 4b shows the growth rates variation in function of hydrogen flow, using the simple pipe as the gaseous mixture inlet.

In all the growth tests, two Raman scattering spectroscopy were done, in the center and in the edge of the sample. The peaks obtained are represented in Figures 5a (center), 6a (edge), in the “shower” shape inlet and in Figures 5b (center) and 6b (edge), in the simple pipe entrance inlet (without “shower”).

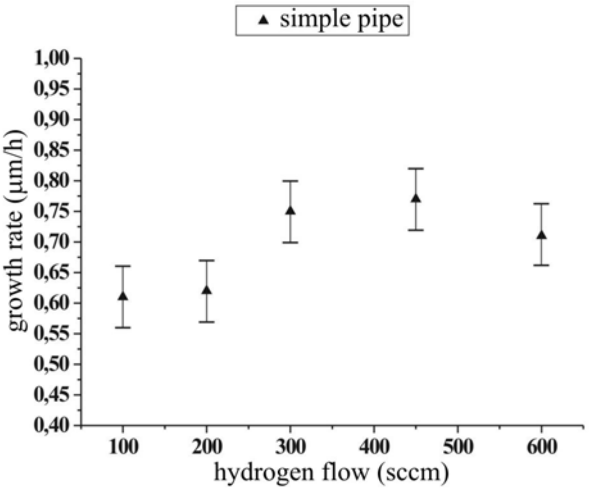

Figure 4b - Growth velocity (μm/h) x hydrogen flow (sccm), using the simple pipe as the gaseous mixture entrance inlet.

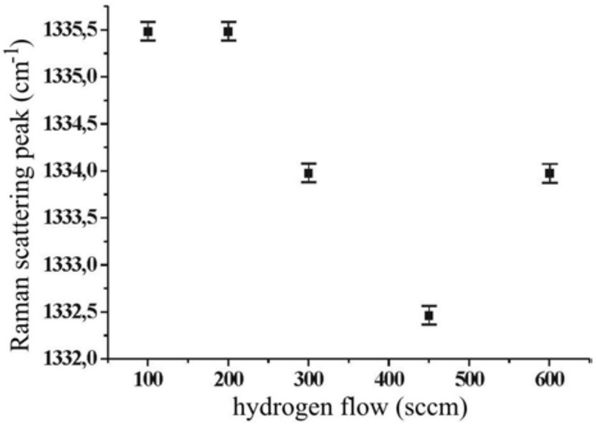

Figure 5a - Raman peak in the central position in function of H_2 flow in the “shower” shape inlet.

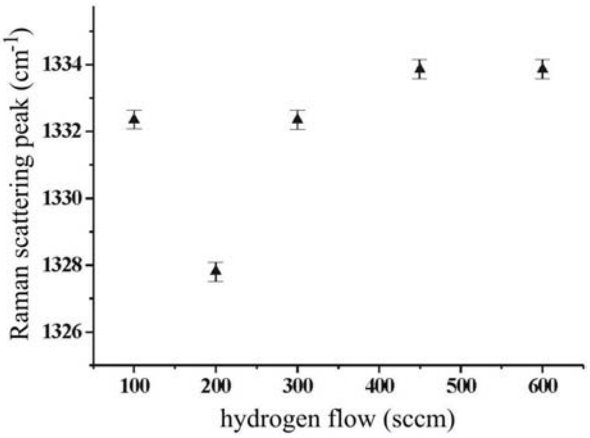

Figure 5b - Raman peak in the central position in function of H_2 flow in the simple pipe shape inlet.

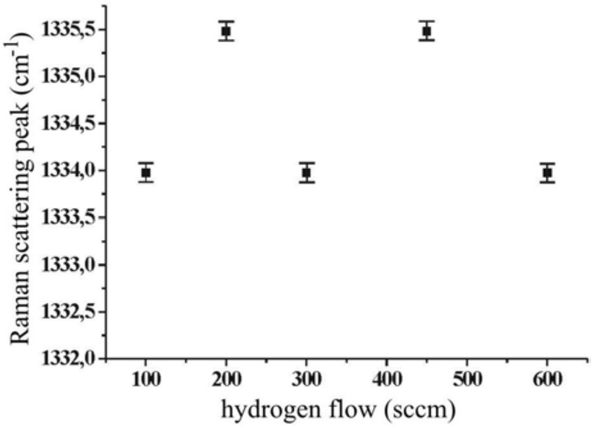

Figure 6a - Raman peak in the edge of the sample in function of H_2 flow in the "shower" shape inlet.

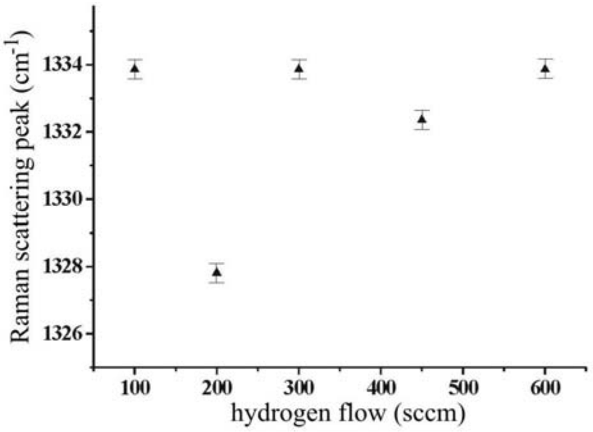

Figure 6b - Raman peak in the edge of the sample in function of H_2 flow in the simple pipe inlet.

In the Raman peak variation analysis, it was observed that there was variation above and below 1332 cm^{-1} in the grown samples. However, except for the growth at 200 sccm of hydrogen flow, using the simple pipe inlet, all the others samples present peaks that are slightly above 1332 cm^{-1}. In this way, comparing the obtained results to the natural diamond of reference without stress, centered peak at 1332 cm^{-1}, we noticed that the stress in the grown diamond was slightly compressive [12]. Figure 7 shows a schematized drawing of the stress process suffered by the samples.

3.2. Establishing limits of diamond growth capacity in present developmental conditions

Success was obtained in the growth for 30 hours of a diamond film, in the conditions previously established: total electric current intensity in the filaments equal to 60.0 A, reactor chamber pressure equal to 50.0 mbar and number of used filaments equal to 15, with 100 sccm hydrogen flow, entering the HFCVD reactor by the simple pipe (without shower). Figure 8 shows a grown sample photograph.
SEM photograph in the central and in the edge parts of the grown sample fragments during 30 h was done. Figures 9a and 9b show, respectively, regions of the central and the edge parts of the sample.

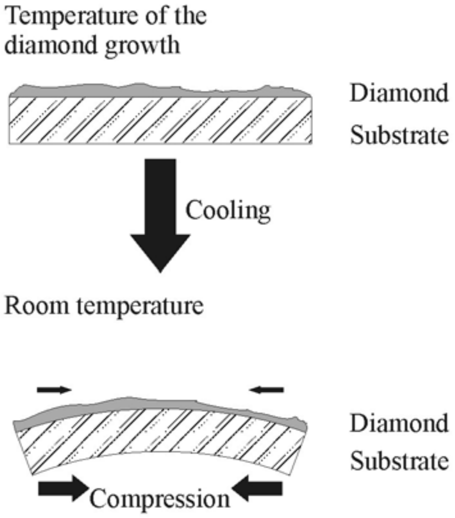

Figure 7 - Stress due to compression [12].

Figure 8 - CVD diamond sample grown for 30h.

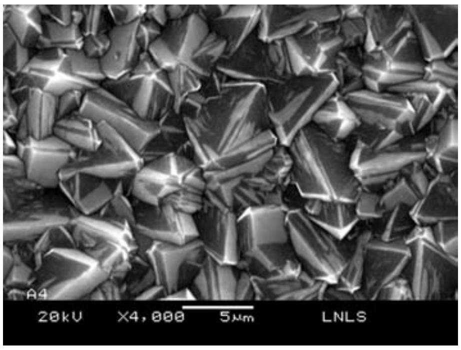

Figure 9a - SEM photograph in the central part of the sample.

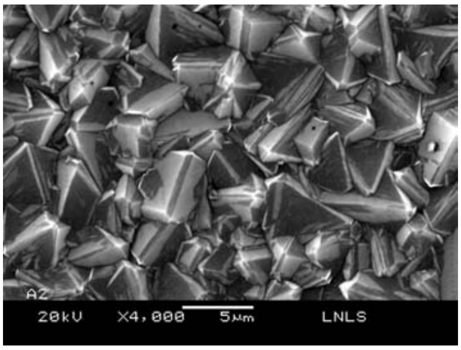

Figure 9b - SEM photograph in the edge part of the sample.

The two final growths were done, intending to evaluate the maximum time limit of the diamond film growth that can be grown without harm over a silicon substrate (100) of 4 inches in diameter and 250 μm in thickness.

The H_2 100 sccm and CH_4 2,0 sccm flows were used. Fifteen filaments were used, the total electric current intensity equal to 64 A and the pressure in the reactor chamber equal to 50 mbar. In the first attempt, the substrate broke with 50 hours of growth. In the second one, the diamond film was grown at the same conditions, but with a deposition time of 70 h. But the substrate and the film split and detached. The diamond film final thickness is 69 μm and the growth rate is next to 1μm/h. Figures 10a and 10b show the samples and the substrates grown final state.

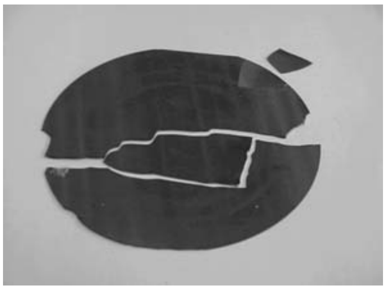

Figure 10a - 50 hours growth.

Figure 10b - 70 hours growth.

As a result of these essays, the obtained values of the growth maximum duration can be presented as the arithmetic average and the sampled pattern deviation of (60 ± 14) hours. However, the associated uncertainty is relatively big due to the small number of realized essays. Another point to be considered is that the film and the substrate destructions were done during the growth process. One might remember that when the sample and the substrate cool, heat different contractions of the grown CVD diamond and the used silicon substrate will occur. So, we can't be sure that samples with 60 hours of duration in the growth process are possible to be obtained.

CONCLUSION

The diamond measured growth rate, (0,7 ± 0,10) μm/h is low for the economical viability process. The Raman scattering spectroscopy analysis shows clearly a good quality diamond growth, in an 80cm^2 area, with minimum compressive stress. The optimum conditions are:

To obtain the growth of minimum cost condition of gaseous mass, one might opt for 2,0 sccm of methane and 100 sccm of hydrogen flows. It is a condition that allows, with the observation of Raman peak, growths with minimum stress.

To obtain the growth in a maximum rate growth condition of diamond film, one might opt for 9,0 sccm methane and for 450 sccm hydrogen flows.

On both cases, one might utilize the simple pipe as the inlet in the HFCVD big reactor because there is a bigger variation in the Raman peak for these flows when the “shower” shape inlet was utilized.

The properties and the diamond growth rates in the surfaces of the used substrate were uniform. The reached development allows diamond growth at 30 μm in thickness in 80 cm^2 areas without breaking the substrate.

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