

Phonon confinement model applied on the Raman spectra of CVD diamond films grown through graphite etching

Modelo de confinamento de fônons aplicado ao espectro Raman de filmes de diamante CVD crescidos através do ataque a grafite

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Abstract

Diamond films, in micro and nanocrystalline (MCD and/or NCD) domain, were grown on silicon substrate 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. Scanning electron microscopy (SEM) images were used to analyze the nucleation rate of diamond films. The films grown during 15 min at 600 and 700°C presented the higher nucleation rate with grain size in a sub micrometer dimension. The high density of NCD formation in the first stage of film growth is attributed to the high amount of available carbon, even from this process governed by the graphite hydrogen etching. Micro-Raman spectroscopy demonstrated the feature of NCD coating, particularly the peak at 1150 cm⁻¹ is attributed to trans-polyacetylene (t-Pa). Also, this high amount of NCD population in such diamond films induces a broadening and shape changes in Raman peak at 1332 cm⁻¹. This behavior was studied from phonon confinement model and the NCD crystallite size was evaluated in the range of 18.5 up to 14.3 nm as the in-plane correlation length L_a .

Keywords: Diamond CVD, Phonon confinement model, Raman spectroscopy.

Resumo

Filmes de diamante micro e nanocristalino (MCS e/ou NCD) foram crescidos sobre substrato de silício. A fonte de metano destes filmes foi obtida via ataque a grafite em uma mistura de hidrogênio atômico. Uma placa de grafite foi usada como suporte para o filme sendo empregado o método de deposição química na fase vapor por filamento quente. Imagens de microscopia eletrônica de varredura foram utilizadas para analisar a taxa de nucleação dos filmes. Os filmes crescidos por 15 min a 600 e 700°C apresentaram uma alta taxa de nucleação com tamanhos de grãos em micro dimensões. A alta densidade para formação dos NCD no primeiro estágio de crescimento dos filmes foi atribuída a alta quantidade de carbono disponível para o crescimento. Isto acontece mesmo em um processo de ataque do hidrogênio atômico a grafite. Espectroscopia Micro-Raman demonstrou um pico característico de NCD, a 1150 cm⁻¹. Este é atribuído ao transpoliacetileno (t-Pa). Também, o grande teor de NCD em filmes de diamante é responsável pelo alargamento e mudança na forma do pico Raman em 1332 cm⁻¹. Este comportamento foi estudado a partir do modelo de confinamento de fônons o que permitiu ainda, avaliar precisamente o tamanho de grão dos nanocristais, que apresentaram tamanho na ordem de 18,5 a 14,5 nm, o que segue relacionado com o comprimento de correlação L_a .

Palavras-chave: Diamante CVD, Modelo de confinamento de fônons, Espectro Raman.

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Introduction

Chemical vapor deposition (CVD) has been shown a very suitable technique to change the deposition parameters for promoting the transition between microcrystalline diamond (MCD) to nanocrystalline diamond (NCD) films. In general, the control of Ar or CH₄ has permitted to obtain the NCD or MCD by altering the presence of sp² at the grain boundary^(1,2). Independently of the procedure, CVD diamond involves two distinct stages; nucleation and growth. In this sense, the use of a solid carbon source becomes an alternative method to investigate how the high amount of carbon on the growth surface, which can be generated by the atomic hydrogen etching, that contribute for each stage of diamond formation. In addition, diamond microstructure control has demonstrated to be essential to obtain the nucleation rate. Traditionally, nucleation for CVD growth of diamond has been aided by a step that involves the substrate scratching producing residual diamond particles as a seeding process. Some authors^(3,5) have discussed the increase of diamond nucleation density associated with high quality film formation when graphitic carbon is presented on the growth surface. Otherwise, there are some authors in the literature that have already produced diamond without using hydrocarbon in the gas inlet. Chow et al.⁽⁶⁾ have demonstrated that the chemical reaction products in the atomic hydrogen-graphite reaction can be used as an efficient starting material for diamond growth. Yang et al.⁽⁷⁾ have found high growth rate of high quality diamond through graphite etching using different setups for graphite and substrate inside the reactor. Diamond films growth with high nucleation rate on silicon substrate from graphite as a carbon source is presented. The Si substrate is kept on graphite plate mounted in the support with a well controlled heating system for ensuring an uniform temperature distribution during the experiments. The Raman spectra for a series of CVD diamond thin films is also studied observing the correlation between the line shift and width of diamond Raman line based on the phonon confinement model.

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 μm diamond powder dissolved in hexane during 360s. A graphite plate was used as sample support in a hot filament chemical vapor deposition reactor. Sample support was mounted for

keeping the graphite and silicon sample about 3.10⁻³ m above 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 3.5.10⁻³ m x 10⁻³ m with 5.10⁻³ m thickness. Graphite plate temperature was measured by a k type thermocouple situated in its central region from a small hole. The growth parameters were hydrogen flux of 100 sccm for a deposition pressure of 26.7.10² Pa at four different temperatures of 600, 700, 800 and 900°C, during 9.10²s to analyze only the nucleation rate. The graphite plate was polished with a silicon carbide paper 1200 grid before each experiment to ensure similar graphite surface for all experiments. Diamond films morphologies were studied from images obtained by JSM310 Jeol equipment. A Renishaw 514.5 nm Raman system was used to carry out diamond films spectra. Five points in the sample were chosen in a central area of 4.0.10⁻⁶ m². For each point in such area, the spectra were scanned five times, in order to improve the statistics of Raman data.

Results and Discussions

Diamond films morphology may be observed in Fig. 1 from top view SEM images considering the growth time of only 9.10² s. Samples produced at 600 (not shown) and 700°C presented similar coatings where the most part of the Si substrate is covered with diamond agglomerates, characteristic of the coalescence process in advanced stage evidencing the high nucleation and growth rates as shown on Fig. 1a. Accentuated nucleation decrease and grow rate are observed at 800 and 900°C (not shown), that present only small grains amount covering the Si surface in the first growth stage, without coalescence process as shown on Fig. 1b. The nucleation rate was not calculated, but it is higher than 109 particles/cm², because the grain size is in sub micrometer range.

Raman spectroscopy has demonstrated to be a convenient and non-destructive tool to characterize carbon materials because each carbon allotrope displays clearly identifiable Raman signatures. Figure 2 depicts a Raman spectrum for diamond film formed at 700°C, concerning sample morphology showed in image 1a. For a better examination, the spectrum was deconvoluted in its different components of sp² and sp³ phases. The principal crystal diamond signature at 1333 cm⁻¹ and the others four separated peak located at around 1150, 1350, 1500 and 1580 cm⁻¹ are clear. The peaks at around 1150 and 1500 cm⁻¹ always appear in NCD films and were recently attributed to

trans-polyacetyline (t-Pa)⁽⁸⁾. The peaks at 1350 and 1580 cm⁻¹ are the popularly known D and G bands.

As discussed above, such films presented a high nucleation rate and, so, a high population of NCD grains confirmed by Raman spectra. Particularly, the sample grown at 800 and 900°C has presented a more evident NCD population with defined regions of well defined grains. This behavior is attributed to the lower growth rate that did not lead to the film coalescence. However, the spectra of diamond crystals, in different size, may be calculated by phonon confinement model^(9, 10). The

phonon confinement model⁽¹²⁾ is based upon the fact that, in an infinite crystal, only phonons near the center of the Brillouin zone ($q \sim 0$) contribute to the Raman spectrum. On the other hand, in a finite crystal, phonons can be confined in space by crystal boundaries or defects and the uncertainty in the phonon momentum allows phonons with ($q \sim 0$) to contribute to the Raman spectrum. The Raman line shape is calculated by superimposing Lorentzian line shapes centered at $\omega(q)$, weighted by the wave-vector q uncertainly caused by the confinement⁽⁹⁾ as Eq. 1:

$$I(\omega) = \int_0^1 \frac{\exp(-q^2 L_a^2 / 4)}{(\omega - \omega(q))^2 + (\Gamma/2)^2} 4\pi q^2 dq \quad (1)$$

where $\omega(q)$ is an approximate one-dimensional phonon dispersion curve, q is expressed in units of $2\pi/a$, and the crystallite sized L_a in units of a , with $a = 3,567 \cdot 10^{-10}$ m being the lattice constant of diamond. L_a was assumed as the correlation length or the theoretical crystal size. For the dispersion curve $\omega(q)$ it is assumed the following form:

$$\omega(q) = A + B \cos(q)\pi \quad (2)$$

where $A = 1193,75$ cm⁻¹ and $B = 139,25$ cm⁻¹. The calculated Raman line shapes for diamond particle sizes are shown in Fig. 3. Open circles and solid lines display experimental data for the natural diamond and the calculated lines, respectively. The fitting program developed in the previous work⁽¹¹⁾ was adjusted for diamond films. As the crystallite size decrease the line broadens asymmetrically and the maximum shifts to lower frequency. The behavior is also similar to that calculated for diamond powders with size less than $2 \mu\text{m}$ ⁽¹³⁾.

Figura 4 shows the results of experimental and calculated data, using the Eq. 1, for the diamond coatings formed at the four temperatures studied, showing the associated crystallite sizes for NCD population between 18.5 and 14.3 nm, correspondent to samples grown between 600 and 900°C. As the crystallite size decrease, the Raman line becomes broader and more asymmetric. The calculated/experimental line widths are between 8.0 and 10.0 cm⁻¹ while for natural diamond is 4,5 cm⁻¹. The phonon confinement model predicts strongly asymmetric line shapes at values of L_a less than about 10 nm. However, the observed spectrum is symmetric, as can be seen in the Fig.4.

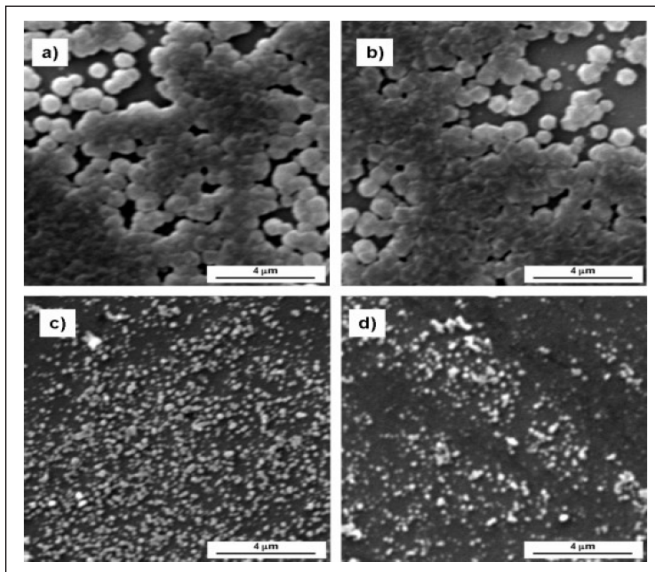


Figura 1. SEM images of diamond films on Si substrate with growth time of 15 min at (a) 700 and (b) 800°C.

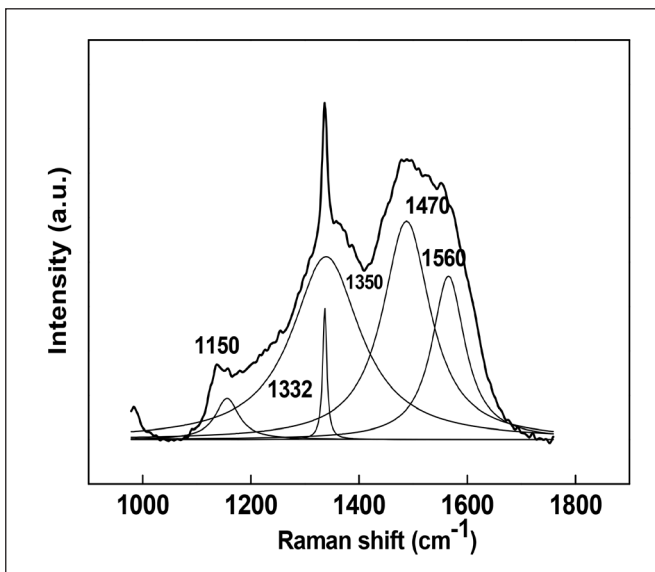


Figura 2. Raman spectrum of diamond film grown for 15 min at 700°C

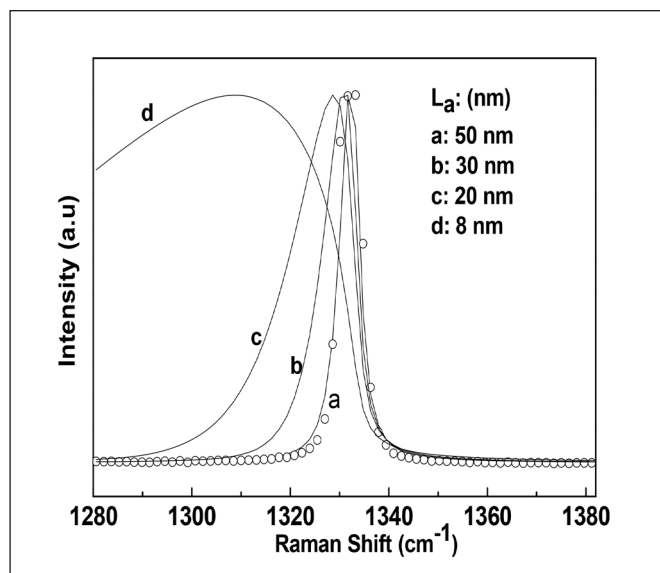


Figure 3. Calculated Raman line shapes for different diamond particle sizes.

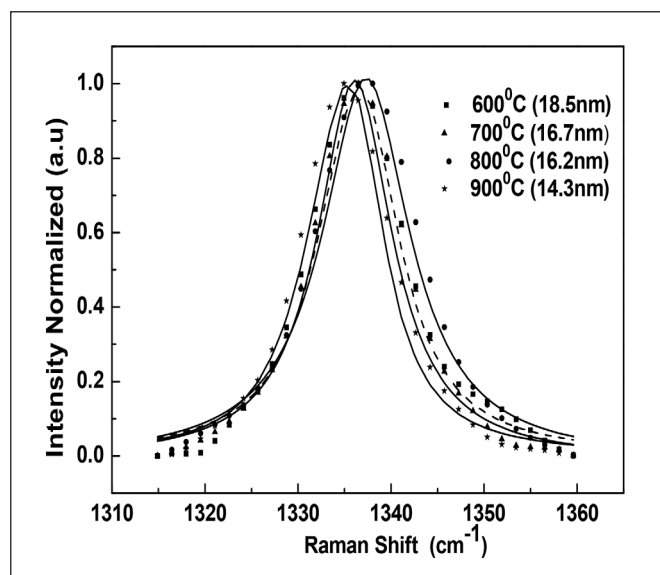


Figure 4. Experimental (symbols) and fitting curves calculated (continuous lines) from phonon confinement theory for samples at 600, 700, 800 and 900°C

Because the diamond line shapes are much more symmetric than predicted by the model the line-width broadening for the films in this study does not arise only from phonon confinement. The disagreement between the observed and calculated line shapes for a given line-width become more evident at smaller values of L_a . The lack of agreement between the line shape and the phonon confinement model leads to consideration

that the strain caused by compressive stress may be the cause of the Raman shift and the broadening.

Conclusion

Homogeneous MCD and NCD films were grown on Si substrate from graphite etching as a carbon source with atomic hydrogen instead of using conventional hydrocarbon in the feed gas. The films presented high nucleation and growth rates for graphite temperatures lower than 700°C even with only 15 min of growing. The contribution of NCD population is confirmed by Raman spectra. The phonon-confinement model and the strain caused by compressive stress may be the cause of the Raman shift and broadening

Acknowledgement

This work was supported by Fundação de Apoio a Pesquisa do Estado do Bahia (FAPESB) and Universidade do Estado da Bahia (UNEB)

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