

## Bias enhanced nucleation process of polycrystalline diamond films.

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We have studied the bias-enhanced nucleation process in the deposition of diamond films by Microwave Plasma Assisted Chemical Vapor Deposition Process (MWCVD). We have found a clear dependence between the nucleation time and the surface morphology of the polycrystalline diamond films whereas the chemical composition remains unalterable. Smooth surface diamond films are obtained applying long bias enhanced nucleation processes prior to growth step.

**Keywords:** diamond films, BEN process, roughness, AFM.

### 1. Introduction.

A limiting stage of the diamond films growth process is the formation of the diamond nuclei. Nowadays, a common procedure to enhance the formation of diamond nuclei consists in the application of a negative bias voltage to the substrate immersed in a plasma containing hydrogen and carbonaceous species, so that the ions are accelerated towards the substrate.

This is the so-called bias enhanced nucleation process (BEN), carried out for the first time by Yugo et al. [1], widely used, but still poorly understood from the physics standpoint [2-4]. A model was previously reported by this group that explains the nuclei formation on top a graphitic layer with basal planes perpendicular to the surface substrate [5]. This model helps to understand the nucleation process.

As it has been extensively reported, diamond exhibits a lot of unique properties which make diamond films a promising material for many industrial applications [6].

One example, due to the tribological properties, is the diamond films use as protective layer that, nowadays, is one of the most investigated technological application. In this sense, the major condition of the diamond films is the low roughness. Some years ago, Stoner et al. [7], and others researches [8], proposed a method to obtain heteroepitaxial, with (100) orientation, diamond films, that consists in three growth steps (carburization, nucleation and properly growth).

These films have got a low roughness. However, the procedure is complex and it strongly depends on the experimental system. An alternative and simpler process to would be the growth of diamond films with very small crystallites, that would correspond to films with low roughness.

In this work we show it is possible to obtain good quality (diamond content >95%) diamond films with very low roughness, only with a two steps method (nucleation, applying the bias enhanced nucleation process, and growth) just controlling the bias enhanced nucleation time.

### 2. Experimental details

Diamond nuclei were grown in a 2.45 GHz ASTEX Microwave Plasma Assisted Chemical Vapor Deposition (MWCVD) system over (100) silicon wafers. Nucleation was enhanced applying a DC voltage, -250 V, to the substrate through the thermocouple sheet, immersed in a CH<sub>4</sub>:H<sub>2</sub> (12:288) plasma at 17 Torr and 450 W. The substrate temperature was held constant at 850 °C. The growth stage was carried out during one hour at 1200 W, 40 Torr, 900 °C, and a gas mixture of 0.5% CH<sub>4</sub> in H<sub>2</sub>.

The morphology of the films was characterized by Atomic Force Microscopy (AFM), using a Nanoscope III system operating in the tapping mode at ambient conditions, and by Scanning Electron Microscopy (SEM), using a Hitachi S-2700 model. The XANES experiments were performed at the Lawrence Livermore National Laboratory/University of California (LLNL/UC). The procedure has been explained elsewhere [5, 9]. Also, the samples were analyzed by Raman spectrometry, with a DILOR x-y Raman spectrometer in the range 1200-1800 cm<sup>-1</sup>.

### 3. Results.

Samples obtained after 5, 10, 15, 19 and 20 minutes of nucleation process were analyzed by AFM [9]. The AFM images showed protrusions on the surfaces that were identified as diamond nuclei.

The chemical characterization of the samples were carried out by XANES [9]. The diamond/graphite ratio (calculated from XANES spectra) increases with nucleation time, as bright spots in AFM images, which confirms the diamond character of protrusions.

From AFM images the nuclei density has been measured and plotted versus nucleation time in Figure 1. It can be observed that, after a delay time where no diamond nuclei are detected, the nucleation density exponentially increases with time, until 20 minutes of pre-treatment, when it saturates. In this case AFM image shows a continuous film. As it was mentioned in Experimental paragraph, the diamond films were grown during one hour after the nuclei characterization.

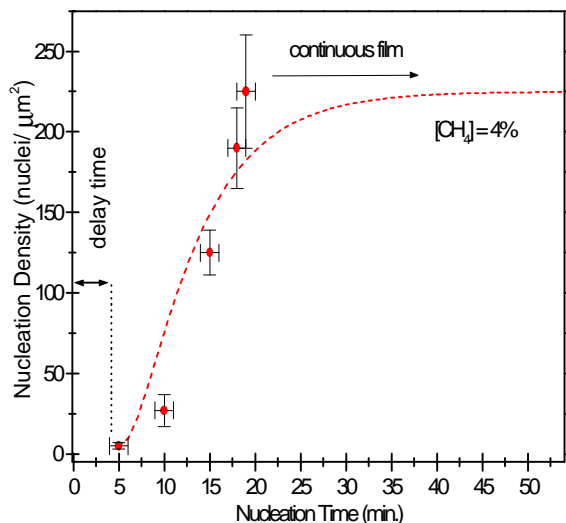


Figure 1. Evolution of nucleation density, calculated from AFM images, with bias-enhanced nucleation time (scattered points) and fit of experimental nucleation data to exponential function

Subsequent to the growth stage the samples morphology was analyzed by SEM and AFM.

The SEM surfaces images of two samples, grown over nuclei formed with different bias enhanced nucleation time (5 and 20 minutes), are presented in Figure 2. Firstly, it can be observed in Fig. 2(a) and (b) that a continuous and smooth film is obtained with this procedure, even with only 5 minutes of BEN process. Moreover, the 2” silicon wafer was entirely covered by a film that looks like the SEM image show here. Besides, as we can observe in Fig. 2(c), which represents a zoom of Fig. 2(a), diamond grains are highly crystalline.

In order to have more quantitative morphology values, from the AFM images of the films the rms roughness, the grain size, the percentage of the covered area and the grain density have been calculated and the results are presented in Table I.

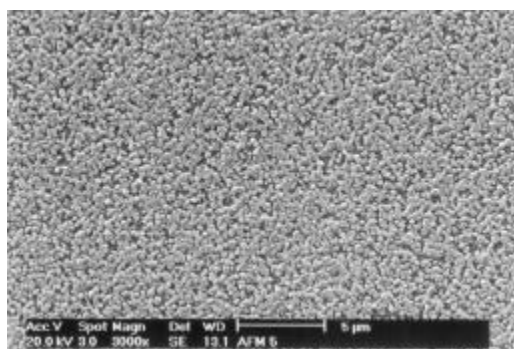
The first important result is the percentage of covered area that, in all cases, even for nuclei formed after 5 minutes, is higher than 95% of the wafer surface, i.e. a continuous film is deposited after one hour of growth

Table I. Morphology parameters of 1 hour grown diamond films over nuclei formed with different BEN time, calculated from AFM images.

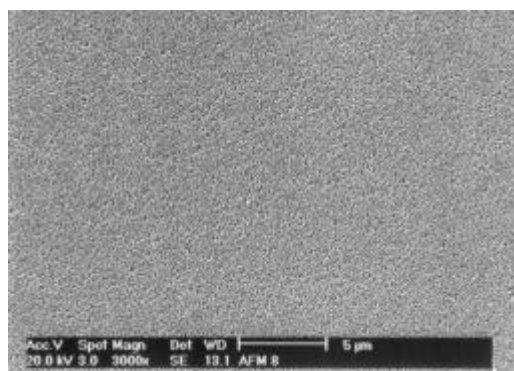
Nucleation Stage		Nucleation + 1 h. Growth			
Nucleation Time (min)	Nuclei per mm² (r <sub>N</sub> )	rms (nm)	Grain Size (nm)	Covered Area (%)	Grains per mm² (r <sub>G</sub> )
5	5±2	69±6	440±40	95±2	6±2
10	27±4	55±5	380±35	95±4	10±3
15	125±20	52±5	300±30	99.8±1	14±3
20	film	15±2	130±10	film	film

stage. This result is very interesting because, as it is known, the diamond film deposition rate at these growth conditions, but without bias-enhanced nucleation, is very low.

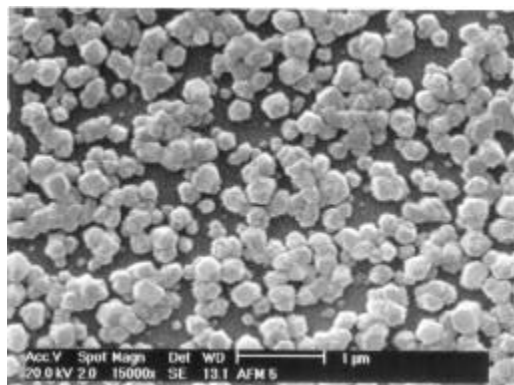
Also, we can observed that both the rms and the grain size decrease, as nucleation time increases, suggesting that it is possible to obtain smooth diamond films applying large nucleation processes. At last, the grains density after the growth stage also increases as the BEN time increases, this number being equal or sometimes minor than nucleation density. This fact indicates that some of the nuclei collapse during the diamond film growth.



(a)



(b)



(c)

Figure 2. SEM images of diamond films grown over nuclei formed with different bias enhanced nucleation time: (a) 5 minutes and (b) 20 minutes, and a zoom image of Fig. (a).

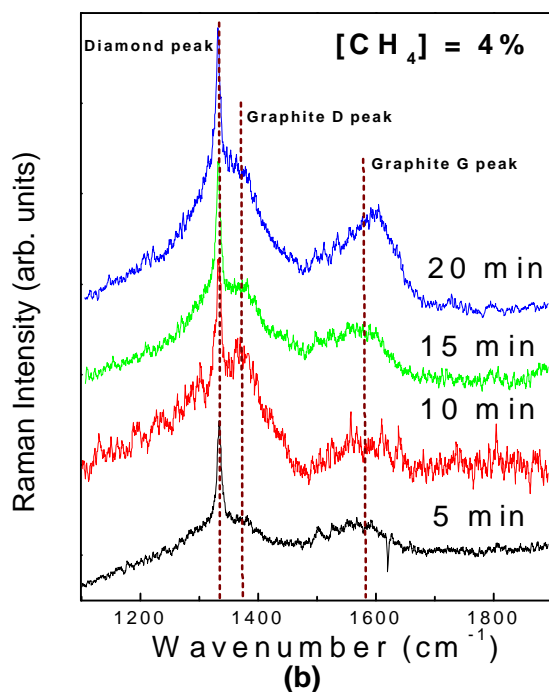
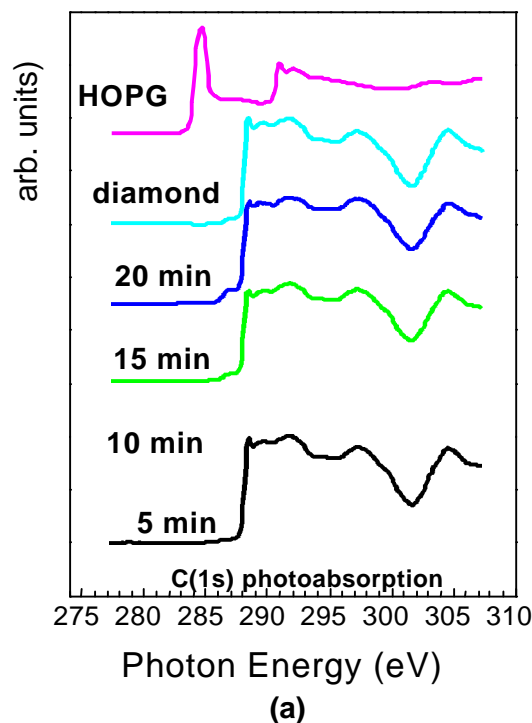


Figure 3. (a) Raman, and (b) C (1s) XANES spectra of diamond samples grown over nuclei formed with different BEN time, and, also in Fig. (b) reference spectra from diamond, and graphite (HOPG).

Finally, the one hour grown diamond films were chemically characterized by Raman and XANES spectroscopies. In this way, information about the bulk (provided by Raman Spectroscopy) and the surface (provided by XANES) of the samples are obtained.

Raman and XANES spectra are shown in figure 3(a) and (b), respectively.

Raman spectra of all the samples show the diamond characteristic peak at  $1332\text{ cm}^{-1}$ , the microcrystalline graphite D and G peaks at  $1340$  and  $1390\text{ cm}^{-1}$ , respectively, and a wide band at  $1500\text{ cm}^{-1}$ , attributed to amorphous carbon. The spectra were deconvoluted, following a procedure already described [10], to obtain the diamond content of the samples. In all the samples the diamond percentage was upper 90%.

Figure 3(b) displays the XANES spectra of the diamond films and reference spectra from natural diamond and Highly Oriented Pyrolytic Graphite (HOPG). The HOPG spectrum presents two characteristic peaks at 285 and 292 eV due to resonances in the  $1s \rightarrow \pi^*$  and  $1s \rightarrow \sigma^*$  transitions, respectively [11, 12]. The major characteristic of the diamond spectrum is the absorption edge at 289 eV. The samples spectra are very similar, with the characteristic features of diamond and without any graphite feature. Thus, from XANES results we can conclude that diamond films surface consists uniquely in diamond phase.

#### 4. Discussion.

From our study of the BEN process, first, we have found there is a delay time of  $\sim 4$  min before the first diamond nuclei are observed, see Fig. 1. In a previous work [5] we have related this delay time to the previous formation of a graphitic layer over diamond nuclei are formed. After the delay time, the nucleation density depends exponentially on the BEN time up to 20 minutes of nucleation process when it saturates.

Tomellini et al. [13] suggested this kind of nucleation behavior is according to a nucleus formation mechanism following the sequence active site-germ-nucleus. The nuclei are effectively diamond, as confirmed by XANES measurements, where the diamond percentage of the samples also increases with the BEN time.

Finally, the formation of the nuclei stops when the surface is fully covered with diamond (a continuous film appears in AFM images), which corresponds to the saturation of the nucleation density in Fig. 1.

With relation to 1 hour grown diamond films, we have observed the diamond films morphology changes with BEN time, but chemical composition, in the bulk (Raman measurements) and in the surface (XANES spectra), remains also constant, with a diamond content higher than 90% in all the samples. The variation of the surface morphology of the samples can be explained by the decrease of the rms roughness, and the grain size in the 1 hour grown samples as the BEN time increases.

These facts, together with Raman and XANES results, suggest that nucleation process influences on morphology features of the film but does not in the chemical nature, and it is very interesting because it is possible to obtain smooth diamond films only by applying long BEN process. Focusing in the production of good quality diamond films, the nucleation step should be stopped just when a continuous film is formed, since subsequently the graphite content in the films would become too high.

Thus, it is necessary to reach a compromise between the final roughness and the quality of the diamond films. Finally, we have observed that in our experimental conditions the best results are obtained stopping the nucleation stage after 20 minutes, when a continuous film has been just formed.

## 5. Conclusions

In this work we have studied the bias enhanced nucleation process of polycrystalline diamond films by afm, xanes and raman spectroscopy. In relation to the effect of bias-enhanced nucleation time, large deposition rates can be obtained even for short treatment time (5 minutes). it has been also detected a dependence between the nucleation time and the surface morphology of the diamond films, in such a way that diamond films with smooth surface can be deposited applying to the silicon substrate a negative bias for long time.

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## References

- [1] S. Yugo, T. Kanai, T. Kimura, and T. Muto, *Appl. Phys. Lett.* **58**, 1036 (1991).
- [2] B.R. Stoner, G.-H. Ma, S.D. Wolter, and J.T. Glass, *Phys. Rev. B* **45**, 11067 (1992).
- [3] X. Jiang, K. Schiffmann, and C.-P. Klages, *Phys. Rev. B* **50**, 8502 (1994).
- [4] R. Stöckel, M. Stammer, K. Janischowsky, and L. Ley, *J. Appl. Phys.* **83**, 531 (1998).
- [5] M. M. García, I. Jiménez, O. Sánchez, C. Gómez-Aleixandre and L. Vázquez sent to *Phys. Rev. B*.
- [6] R.F. Davis, *Diamond Films and Coatings*, (Noyes Publications, New York, 1993).
- [7] B.R. Stoner, S.R. Sahaida, J.P. Bade, P. Southworth, and P.J. Ellis, *J. Mater. Res.*, **8**, 1334 (1993).
- [8] P. John, D.K. Milne, P.G. Roberts, M.G. Jubber, M. Liehr, and J.I.B. Wilson, *J. Mater. Res.*, **9**, 3083 (1994).
- [9] M. M. García, L. Vázquez, I. Jiménez, C. Gómez-Aleixandre, J. M. Albella, O. Sánchez, L.J. Terminello and F.J.Himpfel, *Appl. Phys. Lett.* **72**, 2105 (1998).
- [10] M.M. García Poza, M. Hernández-Vélez, C. Gómez-Aleixandre, J. Sánchez-Olías, A. Blanco-Montes, and J.M. Albella, *Mater. Lett.*, **29**, 111 (1996).
- [11] J. F. Morar, F. J. Himpfel, G. Hollinger, J. L. Jordon, G. Hughes, and F. R. McFeely, *Phys. Rev. B* **33**, 1346 (1986).
- [12] P. E. Batson, *Phys. Rev B* **48**, 2608 (1993).
- [13] E. Molinari, R. Polini, V. Sessa, M.L. Terranova, and M. Tomellini, *J. Mater. Res.* **8**, 785 (1993).