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# ***Synthesis of highly oriented CVD diamond films by ultra short bias enhanced nucleation step***

S. Barrat, S. Saada, J.M. Thiebaut, E. Bauer-Grosse

## **Introduction**

Highly oriented diamond films deposited by chemical vapor deposition (CVD) processes have focused interest of many research groups ten years ago (see for this purpose the review paper [1]). This interest is mainly due to the perspective of large industrial developments of deposited heteroepitaxial diamond coatings whose crystalline quality must approach the natural diamond quality. The nature of the substrate mainly depends on the type of envisaged applications, however the single silicon wafer constitutes unquestionably the largest material used because large single crystals are available at low cost and present some similitude with diamond. The CVD synthesis of heteroepitaxial diamond deposits is mainly due to the development of an *in situ* substrate pretreatment so called Bias Enhanced Nucleation (BEN) initially presented by Yugo et al.[2], Jiang et al.[3], and Stoner et al.[4]. This procedure is carried out before the diamond growth step with close experimental conditions, leads to a very important increase in the nucleation density and then, by optimizing the bias conditions, to an epitaxial relation between the diamond crystals and the silicon substrate. The final goal of many studies is to induce highly oriented films mainly constituted by epitaxied crystals. The morphological characterization of the film surface does not allow to correctly evaluate this state since evolutionary selection rule leads to the elimination of misoriented crystals during thickening. It is necessary to determine the epitaxial ratio which can be defined as the percentage of epitaxied crystals in relation to the total crystal number before the texture formation. Classically, highly oriented diamond films are obtained from an epitaxial ratio of few per cent [4]. The higher it will be, the better the subsequent diamond film quality will be. However, the epitaxial ratio is difficult to increase because of the extreme complexity of the

physical and chemical substrate environment during the pretreatment step. If we restrict this discussion to the most used CVD process, i.e. the microwave plasma assisted chemical vapor deposition (MPCVD) technique, the BEN step consists in superimposing a microwave discharge (which is in contact with the substrate) with a d.c glow discharge created by negative biasing of the substrate relative to the reactor wall (or relative to an additional anode located above the substrate). As studied previously [6-9], the variety of device configurations (size and nature of reactor, shape and size of substrate-holder, electric-field distribution of microwave plasma and d.c bias) and the large synthesis parameter variations (nature and composition of the plasma-producing gas mixture, substrate temperature, microwave power, pressure and bias conditions) lead to a high dispersion of results in terms of diamond quality, epitaxial ratio, deposit homogeneity and sometimes in term of synthesis reproducibility [6]. This lack of result uniformity does not permit to clearly determine the main mechanisms of diamond formation during the bias step, and the multiple nucleation models presented in the literature illustrate this diversity [4-7,10-16]. Two main aspects can be considered in regard to the BEN step in the case of MPCVD synthesis on silicon substrates: the chemical and electrical behavior of the double-discharge which has been strongly studied [6,8-9,11,14], and the substrate modifications submitted to these discharges that interest many research groups [4-7,10,12-19] and whose knowledge constitutes today a real stake for the optimization of this process. The later aspect is particularly sensitive because the substrate transformation during the bias is mainly linked to the temperature that generally varies between 800 K and 1200 K, and to the duration comprised between 20 s and 2 hrs. For shortest time nucleation homogeneity is poor [20] and to preserve a high nucleation density, the BEN step is often preceded by an *in situ* carburation step. Therefore in some cases, silicon substrates undergo large transformations whose sequence is difficult to analyze. The study of these transformations is all the more complicated than the nucleation process often occurs heterogeneously with time and location. Consequently some studies are based on the variations of the diamond deposit quality along the substrate surface [6,8,16,19-

26].

In this context, to facilitate the understanding of the physical and chemical mechanisms which occur during the bias step, our main goal is to find experimental conditions for which deposits are uniform and reproducible in order to easier correlate the macroscopic parameters of the process to microscopic phenomena related to the nucleation mechanisms independently of the location on the substrate. Our second objective is to determine the pretreatment the simplest as possible to eliminate steps of the process which seem not necessary for nucleation and orientation of the diamond crystals. This two points are discussed below then characterizations of two deposits are presented.

## **Results and discussion**

### ***Control of the double-discharge***

As predicted by previous studies [24,27], increasing homogeneity requires a strict control of the double-discharge. We have recently described the interaction between the microwave plasma and the d.c discharge [9] and demonstrated that the d.c discharge homogeneity was directly linked to the microwave location over the substrate/substrate-holder system and to the electric-field distribution of the d.c voltage. Concerning the last point, a graphite electrode located above the substrate has been added to minimize the d.c electric-field gradient near the substrate-holder. It is important to point out that the distance between the substrate and the electrode must be chosen to avoid microwave plasma disturbance. This condition can be qualitatively foreseen by calculating the electric-field distribution of the microwave wave inside the reactor when the microwave plasma is not initiated yet. This distribution is shown in fig.1 where the vertical axis corresponds to the electric-field intensity and the horizontal axes ( $r,z$ ) define a half-plane of the microwave cavity limited by the substrate-holder (lower part of the plane) and by the microwave antenna (upper part of the plane). For a system with a symmetry of revolution ( $r,\theta,z$ ), the calculation of the

electromagnetic field in TM modes (Transverse magnetic modes) is carried out from the following magnetic excitation relationship:

$$\frac{\partial}{\partial z} \left( \frac{1}{\epsilon_r} \frac{\partial(r.H_\theta)}{\partial z} \right) + \frac{\partial}{\partial r} \left( \frac{1}{\epsilon_r} \frac{\partial(r.H_\theta)}{\partial r} \right) + \frac{(2\pi\nu)^2}{rc^2} (r.H_\theta) = 0 \quad (1)$$

with  $\epsilon$  the relative permittivity of the environment,  $\nu$  the eigen frequency of the cavity and  $c$  the light velocity. The eigenvalue resolution is performed by a finite element method and gives after derivation the electric-field module at each node of the cavity. This one consists to oscillations with the presence of antinodes. We experimentally observed that the introduction of an anode inside these antinodes does not disturb the subsequent microwave plasma initiation and decreases the d.c electric-field gradient near the substrate-holder when the bias is applied. The presence of a high microwave electric-field at the extremities of the substrate-holder is also particularly visible in figure 1. That induces very strong point effects when the microwave plasma is switched on and corresponds to the catching areas usually observed when the microwave plasma is initiated. Its homogeneity is all the more difficult than point effects exist. As presented in a next paper, simulations of the microwave electric-field distribution with various substrate-holder geometries showed that point effects can be strongly decreased for particular shapes. Fig. 2 reports the final configuration of the system substrate/substrate-holder that minimizes the microwave plasma heterogeneity and favors the d.c. discharge spreading over the substrate surface. As described by previous studies [6,9,16], the nature of materials submitted to the bias has an influence on the d.c discharge extension. So it is well known that the bias plasma often starts on the uncovered substrate-holder (molybdenum or graphite in the most cases), then spreads over the silicon substrate with diamond formation. Moreover, the extension of the bias plasma on the surrounding materials constituting the uncovered substrate-holder is detrimental to the BEN reproducibility since successive syntheses lead to a modification of the chemical nature of the substrate-holder by formation of carbides or diamond. To avoid these transformations, we have deposited a thin ceramic coating on the substrate-holder surface (see figure 2) which can be easily replaced, and that prevents

the extension of the bias plasma beyond the silicon surface.

From this new experimental configuration, and for a total pressure comprised between 1 and 40 hPa, the substrate constituted by a square of  $1 \times 1 \text{ cm}^2$  of silicon is well located inside the microwave discharge that appears very homogeneous without point effects. When the voltage is comprised between 80 and 170 volts, the bias plasma spreads instantaneously over the all substrate surface without any visual microwave plasma disturbances. This leads to very homogeneous deposits over the all substrate surface that we have characterized by image analysis [36].

### ***Simplification of the BEN process***

Two approaches can be considered for the simplification of the BEN process. The first one consists to limit the number and the duration of the steps preceding the bias. The second one is to reduce the duration and the intensity of ion bombardment during the bias in order to minimize the modification of the substrate surface while maintaining a sufficiently high nucleation density with an acceptable epitaxial ratio and a good homogeneity. As mentioned by Wolter et al. [23], standard process parameters used in the most BEN steps (medium pressure, hydrocarbon/hydrogen ratio below 5%) must allow to deposit an uniform diamond film with a high nucleation density by using short bias durations. This statement is worth developing since some studies pinpoint that longer bias time leads to an epitaxy loss [7,16,17,28] and a decreasing in the diamond quality [12]. High bias voltages are reported to raise the nucleation density but also the growth of poorly oriented crystallites [20,29].

Concerning the *in situ* pretreatment steps, we have chosen to only keep the hydrogen etching a few minutes before the bias step without preliminary carburation step. This last one is actually very controversial since some studies associated it to the formation of a  $\beta$ -SiC conversion layer [12,17,21,22,30] while others suggested the formation of non diamond phases like amorphous carbon [18] or a combination of both [19,29,31]. Moreover, some studies reported that the bias step

led to the formation of this conversion layer [4-7,10,12,15]. Whatever the substrate transformations during the carburation step, it is experimentally demonstrated that diamond epitaxy can be achieved without this one [8,10,11,13,27-30].

We conserve the hydrogen etching for two main reasons. Firstly the bias step on silicon substrates cannot be started at temperature below 900 K since the efficiency of the bias plasma seems linked to the silicon conductivity. Indeed we observed that a too low temperature induces a wrong extension on the bias plasma and consequently a large heterogeneity of the subsequent diamond deposit. Nevertheless to limit the hydrogen etching duration, we mounted a tungsten coil inside the molybdenum substrate-holder (see fig. 2) which is electrically insulated from this one and heated by Joule effect. This heating device allows us to quickly increase the substrate temperature up to 813 K before the hydrogen etching step. The second reason of maintaining the etching step is the supposed cleaning effect of the hydrogen plasma which is reported to remove the native oxide layer of the silicon [7,11,28,32]. This one is thought to inhibit the nucleation as it is used as masks in selected area nucleation applications [33]. However, this cleaning notion must be taken carefully since the reduction of oxides in a hydrogen plasma seems counterbalanced by the oxidation from residual oxygen present in the classical MPCVD reactor [34]. This aspect is presented in a next paper [35]

### ***Synthesis and Characterizations of the deposits***

From previous considerations and few preliminary attempts, the final synthesis conditions are reported in table 1. Before introducing the silicon substrate into the reactor, it is cleaned in acetone, simmered in trichloromethane and then simultaneously etched and passivated in 40% hydrofluoric acid for 60 seconds. The preheating step is carried out in pure hydrogen and kept until the substrate temperature reaches 813 K. Then, the subsequent hydrogen plasma etching quickly increases the substrate temperature up to 1073 K. This temperature has been chosen because it insures a good bias plasma spreading as soon as its start, but the absolute value of the temperature does not seem to have a strong effect on the epitaxial nucleation [20]. The bias step is performed for 30 seconds with

moderate voltage and methane/hydrogen ratio. The consequence is a very high and uniform nucleation density for a short polarization time so called USBEN for Ultra Short Bias Enhanced Nucleation. We have evaluated the nucleation density to about  $4.7 \cdot 10^9 \text{ cm}^{-2}$  by performing SEM characterizations when the sample has been submitted to a 20 minutes growth step after biasing (fig.3a). Some epitaxial crystals are visible and pointed out by open white circles. Statistical image analysis treatment developed in a previous work [36] shows that the epitaxial ratio is equal to 6% corresponding to an epitaxial crystal density equal to  $2.8 \cdot 10^8 \text{ cm}^{-2}$ . There are few epitaxial crystals in comparison with the total number of crystals, however it is high enough to quickly produce  $\langle 100 \rangle$  highly oriented diamond films via the evolutionary selection rule [36]. Figure 3b shows the morphology of a highly oriented film obtained for identical synthesis conditions of the deposit seen fig.3a, but for a growth step duration of 20 hrs. We clearly observe the selection of epitaxial crystals at the expense of others leading to a homogeneous surface mainly constituted by epitaxial crystals. Concerning the possible mechanism of diamond nucleation during the bias step, we can advance that the very short bias duration with low bias voltage does not strongly modify the silicon substrate but sufficiently to have nucleation and orientation. This is supported by the fact that the average energies of the main hydrocarbon ions during the bias is reported to be comprised between 50 and 100 eV for pressure about 25 hPa [37,38]. In our case where the pressure is fixed at 13 hPa, the ion energy is slightly higher but does not exceed 120 eV. Therefore, the number of displaced silicon atoms due to the impinging ions is about 8.5 [40], that approximately corresponds to a penetration depth of about 1 nm [40,41].

## Conclusions

We improve the homogeneity of the highly oriented diamond films by increasing the localization and the stability of the double-discharge (d.c and microwave discharges). This improvement is carried out by modifying the nature and the geometry of the substrate-holder and by increasing the electric-field homogeneity associated to the d.c polarization. The consequence is a drastic reduction



of the polarization time while maintaining a high nucleation density with an usual epitaxial ratio [5-17] and with a very good homogeneity. This one leads to the synthesis of highly oriented diamond films when a thickening is performed. The weak duration of the ion bombardment with ions having a quite low energy seems to mean that the bias step probably consists to a slight modification of the substrate surface.