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# **TOWARDS HOMOGENEOUS AND REPRODUCIBLE HIGHLY ORIENTED DIAMOND FILMS.**

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## **Abstract**

Diamond films have been deposited by the microwave plasma assisted chemical vapor deposition technique (MPCVD) using an ultra short bias enhanced nucleation (USBEN) step to synthesize highly oriented diamond films on single silicon substrate. First, we focus on the BEN process to obtain homogeneous and reproducible diamond deposits. By optimizing the process, we obtain crystal density value of  $10^9 \text{ cm}^{-2}$  on the whole substrate surface for a reduced polarization time of 60 seconds. Then, using Scanning Electron Microscopy and image analysis, we perform cartographies of crystal densities, covering rate and average radius on the whole sample surface. Second, we analyze a local area of the surface to realize a size distribution of the particles versus their type. Lastly, we discuss about the ratio of epitaxial crystals.

## **1 Introduction**

In order to clarify our purpose, we define a  $\langle 100 \rangle$  texture film as a film which is the result of the evolutionary selection rule [1] from randomly oriented diamond crystals. An highly oriented film is formed by growth under conditions which promote  $\langle 100 \rangle$  texture from epitaxial and randomly oriented diamond crystals. When all the crystals are epitaxied we speak about epitaxial film. Highly oriented diamond films synthesized on non diamond substrate by chemical vapor deposition

(CVD) processes is one of the promising way to obtain diamond coatings whose quality can approach the natural diamond which is too expensive and not obtainable in the shape of films. Some of applications require good chemical and structural qualities especially electronic applications which need single-crystalline structure, low defect density and smooth surface [1]. The CVD synthesis of highly oriented 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.[3], Jiang et al.[4], and Stoner et al.[5]. As studied by several authors [6-9] in the case of the microwave plasma assisted CVD, this process consists in superimposing a microwave discharge with a d.c. glow discharge created by negative biasing of the substrate relative to the reactor wall. With classical BEN conditions, this step leads to a high nucleation density increase with a variable percentage of epitaxial crystals. Unfortunately, the multiple device configurations and the large domain of BEN parameters induce a high dispersion of results concerning the deposit in terms of diamond quality, nucleation density, percentage of epitaxial crystals and more globally in term of heterogeneity. This one can be defined as the dispersion of the microscopic characteristics of the deposit previously cited with respect to the location on the substrate. It is often worsened by long BEN duration and by the subsequent growth step since the microwave discharge is often ball-shaped and induces variations of the power density along the substrate as observed by several studies [10-15]. Therefore, some works integrate this gradient to their characterizations concerning the deposit [7,8,10,11-16,18] or the substrate transformations [12,17]. Independently of the heterogeneity and if we restrict the discussion to the most used substrate i.e. silicon, it is necessary to reach high nucleation density and film thickness more than 5  $\mu\text{m}$  to compensate the poor percentage of epitaxial particles at the initial growth stage [2,19]. This limitation is mainly due to the high proportion of the multiply twinned particles (MTP) which is not very studied although some studies tackle the origin of the twin formation [14,20-22] or the evolution of MTP crystals during the growth [20,23-24].

In order to facilitate the characterization of the first stages of the nucleation step during the bias, we optimize the process to obtain homogeneous and reproducible deposits. The objective of this optimization is to correlate parameters of the process with microscopic characterizations of the deposit independently of the position on the substrate for a better understanding of the nucleation mechanisms. We present some quantitative results concerning the macroscopic homogeneity of samples obtained in a modified microwave reactor which ensures good plasma homogeneity on the substrate and allows to perform ultra short BEN pretreatments since large bias exposure is reported to provoke diamond damaging [5,7,9,25,26]. This shortened step so called USBEN and presented elsewhere [27] is performed for duration lower than 1 minute. That guarantees very weak substrate modifications and induces homogeneous high nucleation densities with a sufficient percentage of epitaxial particles. Besides, it tends to limit the growth of crystals during the bias step and to isolate the nucleation site formation. However, it is difficult to entirely separate the growth from the nucleation step because during the bias step both occurs at the same time except for the incubation time. Therefore by lowering the bias step, we tend toward the incubation time and then we limit the growth during bias. We present results concerning the crystal size distribution in relation to the type of the particles and discuss the possibility to reduce the ratio of non epitaxial crystals.

## **2 Experimental setup**

In this study, highly oriented diamond films are synthesized by the microwave plasma assisted chemical vapor deposition technique using the Bias Enhanced Nucleation step. A complete description of the reactor has been done previously [9,27]. In these studies, we modify the geometry of the reactor cavity and the nature of the substrate holder material to confine the microwave plasma on the silicon surface without point effects and to obtain an uniform d.c. glow discharge on the whole silicon surface.

We choose adequate values of the process parameters to have homogeneous deposits. Although some studies try to determine the best set of parameters (so called “sweet spot”) [11,18], we think that they are strongly dependent on the process configuration and only qualitative evolutions can be performed and extended to other configurations. For example, if the bias voltage is too weak or the total pressure too high, the d.c. glow discharge does not completely cover the substrate and the nucleation is not homogeneous. So values of parameters must be chosen in a range to keep homogeneous deposits. The reproducibility of the BEN experiments has been widely developed elsewhere [9,27]. We have shown that it can be improved choosing relevant parameters (other than classical parameters as tension, current or bias time) to describe the BEN step. Thus, the carbon flux density on the substrate, the preparation of the substrate surface and the modification of the surface substrate holder have been specially controlled.

We have investigated a range of value parameters from this system in order to have not only homogeneity but also highly oriented diamond films. We have chosen in these domains experimental process parameters satisfying both conditions (table 1). The substrate used is a mirror-polished (001) oriented silicon wafer (square of 10x10 mm<sup>2</sup>), cleaned in acetone, simmered in trichloromethane and then chemical etched in 40% hydrofluoric acid for 60 seconds just before the synthesis. It is interesting to note that, with the BEN parameters we choose, a bias time of one minute is sufficient to form a highly oriented diamond film with three hours of growth (fig.1). Then, it constitutes the shortest bias time compared with these ones of the literature. Besides, a drastic reduction of the bias time is still possible with this USBEN step and can be reduced to 15 seconds [27].

### 3 Results and discussion

#### 3.1 Introduction

The correlation between relevant process parameters and microscopic characteristics of the deposit is possible only if the latter is homogeneous on the whole sample surface. In others words their variations as a function of the substrate position must be weak. Therefore, we quantify the variations of several microscopic characteristics of the deposit: the covering rate  $\theta$ , the crystal density  $\rho$  and the average particle radius  $\bar{r}$  on the scale of the substrate to define the macroscopic homogeneity. The process parameters of the studied sample are identical to those reported in table 1 except the growth time which is reduced to 16 min to avoid the coalescence step. In addition, a local analysis has been performed for calculating the particle size distribution versus the particle type.

#### 3.2 Macroscopic homogeneity

We perform this quantitative characterization using a scanning electron microscopy (SEM Philips XL30S-FEG) coupled with an image analysis software (Aphelion, ADCIS S.A.). The surface sample is meshed by a grid pattern defined via the SEM where each node is separated from others by 1 mm. Diamond deposit is characterized at each node by analyzing 5 images which correspond to an area of  $200 \mu\text{m}^2$  ( $\approx 4000$  particles). Then, we determine at each node the average values of the microscopic characteristics. Lastly, the graphic representation of each parameter is made by extrapolating these values to obtain a cartography of the sample.

Fig. 2a represents the cartography of the covering rate  $\theta$ . We show that diamond crystals cover the entire surface and the covering rate is comprised between 30% and 60%. The higher covering rate area is located at the upper right corner. As the deposit is thin enough (short growth duration), it exhibits colors due to interference fringes, which depend on  $\theta$ . The visual aspect of the color outlines fits very well with the covering rate cartography. This result shows that there is a good

macroscopic homogeneity and that the aspect of color fringes gives a good indication of this one. This macroscopic homogeneity can be defined as global because it integrates informations about the homogeneities of the crystal density and the growth rate. In order to distinguish these two contributions, we perform the cartography of  $\rho$  and  $\bar{r}$ . Indeed, the first one is representative of the BEN step if we consider that the crystals appear from nucleation sites created only during this pretreatment, whereas the second one is representative of the growth rate which is function of the microwave plasma homogeneity. This hypothesis is supported by the fact that the growth period is much longer (16 min) than the BEN period (1 min), and that a growth step without previous bias induces a crystal density nearly equal to zero. Fig. 2b represents the cartography of the crystal densities. They are comprised between  $1.10^9$  and  $2.10^9$  cm<sup>-2</sup> meaning that the nucleation is very homogeneous on the whole surface using the BEN process. The higher crystal density area is located at the lower right corner and does not correspond with the higher covering rate defined in fig.2a. Concerning the average particle radius presented in fig.2c, it is comprised between 100 and 600 nanometers. In this case, the higher average particle radius area corresponds roughly to the higher covering rate area and the outlines of fig.2a and 2c are rather similar. So, the weak global heterogeneity visualized in fig.2a is the consequence of a slight variation of the growth rate on the substrate and not of a variation of the nucleation density. To conclude, we can say that the deposit is homogeneous but it persists a slight microwave plasma heterogeneity on the substrate which induces a variation of the concentration of reactive species and then a variation of the diamond growth rate.

### **3.3 Island size distribution and type of particles.**

A specific image analysis software for calculating the particle size distribution versus the particle type has been developed. Each crystal is approximated by a disc presenting the same area on the scanning electron micrograph, and the corresponding particle size is defined as the disc radius. The software permits to distinguish different types of particles: Multiply-Twinned Particles (MTP), non

epitaxial single crystals, epitaxial crystals and undetermined particles. These latter correspond to particles whose shape is not resolved by the microscope or to cauliflower-shaped particles. We can observe these different types of particles in fig. 4. The resulting statistics come from a  $68 \mu\text{m}^2$  area ( $\approx 1400$  particles) located inside the zone ( $x=6;y=2$ ) of the reported cartography in fig.2. Fig. 3 shows the size distributions for three types of particles. The shapes of three curves are similar whatever the particle type is and they present also a tail toward small particle sizes. We have to note that the small shoulder observed for small radii in the case of the single crystal curve is not representative because of the accuracy of the method. Since the growth rate can be considered as identical for each particle at a local scale, it means some crystals nucleate during the growth step. Among these ones, some are epitaxied. If we consider that nucleation sites are only created during the BEN step, the presence of small epitaxial crystals shows that the nucleation from these sites can occur during the growth step. So, the bias step only seems necessary to create nucleation sites which can be the seat of the nucleation of epitaxial crystals during the growth step. This result is supported by the fact that high crystal densities up to  $10^9 \text{ cm}^{-2}$  can be reached with BEN step durations about 15 seconds [27].

### **3.4 Epitaxial ratio.**

We report in table 2 the ratio of each type of particles and the corresponding crystal densities. We define the epitaxial ratio as the number of epitaxial crystals divided by the number of total crystals. We find an epitaxial ratio around 5% which is constant on the whole surface and an associated epitaxial crystal density of  $10^8 \text{ cm}^{-2}$ . It is important to note that similar values of epitaxial ratio on silicon substrate are reported in the literature. In fact, there is very few epitaxial crystals in comparison with the total number of crystals. However the epitaxial crystal density is high enough to quickly produce  $\langle 100 \rangle$  highly oriented films via the evolutionary selection rule [1] for which the epitaxial crystals overgrow the non epitaxial ones during thickening. This procedure does not permit to obtain high quality of thinner epitaxial diamond films since the evolutionary selection rule is



difficult to bring into operation. So, the quality of the epitaxial films could be strongly improved by increasing the epitaxial ratio during the first steps of syntheses. A promising way to do it is the reduction of the MTP ratio which is very high (about 64% in our case) and a reduction of the non epitaxial single crystal ratio (26%). From recent syntheses performed by using the USBEN technique, we think that these ratios can be modified by optimizing again the BEN parameters but also by controlling the etching step before the bias since this etching strongly modifies the nucleation efficiency during the subsequent steps when the bias is short.

## 4 Conclusions

Homogeneous and reproducible highly oriented diamond films have been synthesized by the MPCVD technique using the USBEN step. Using the same experimental conditions, we stop the growth step just before the crystal coalescence and perform a quantitative analysis using image analysis and SEM. We characterize the degree of homogeneity of the deposit in terms of coverage rate, crystal densities and particle average radius by means of sample cartographies. We show that the macroscopic homogeneity is good and that the slight variations come from the growth step. Using a specific analysis SEM image software, we carry out local analyses to determine the size distribution of each type of particles. We show that part of epitaxial nucleation can be produced after the BEN step. From this result and since the BEN step can be very quick, we think that the BEN can only induce nucleation sites that will be the seat of nucleation during the subsequent step . The low epitaxial ratio (5.6 %) is nevertheless high enough to give highly oriented films with a short growth step because the associated epitaxial crystal densities is high ( $9.8 \cdot 10^7 \text{ cm}^{-2}$ ). The production of thinner highly oriented film can be envisaged by a decreasing in the non epitaxial particle ratio which depends both on the etching step and the bias conditions.

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