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MICROWAVE PLASMA ASSISTED CHEMICAL VAPOR DEPOSITION OF DIAMOND

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Abstract - Diamond crystals and polycrystalline diamond films have been deposited by the microwave plasma assisted CVD method from \( \text{CH}_4/\text{H}_2 \) mixtures. The inlet concentration of methane, the pressure, the temperature, the total flow rate and the microwave power were varied in large ranges. The morphology of the deposits were studied by optical and scanning electron microscopy and the structure by X-Ray diffraction and Raman spectroscopy. The morphologies ranging from microcrystalline spherulitic deposits to well-faceted ones with different habits are related to the degree of structural order, the whole being clearly apparent to the experimental deposition conditions. A discussion of the global deposition process is based on the examination of two successive steps, the nucleation and the growth. It is proposed that the important parameter which controls these two steps is the ratio between the concentrations of the hydrocarbon neutrals and the hydrogen atoms at the gas-solid interface. Together with the substrate temperature, the variations of these concentrations allow to represent the influence of all the experimental deposition conditions. Then these interfacial parameters are correlated with the degree of structural order and the stability of the different type of morphology of the deposits. As different combinations of the experimental parameters can lead to the same interfacial deposition conditions, this permits to explain some apparent discrepancies between the results of previous published studies and to deduce some general important characteristics for diamond deposition.

1. - INTRODUCTION

Various methods have been employed to deposit diamond crystals and films. They include techniques where a plasma is generated in the gas phase like capacitively and inductively coupled R.F. plasma CVD, microwave plasma CVD, D.C. plasma CVD or more recently thermal R.F. plasma deposition /1 - 8/. The other principal methods of deposition are the hot-filament assisted CVD and electron-assisted CVD /9 - 12/.
For several of these techniques, especially R.F. and microwave plasma CVD, hot-filament and electron-assisted CVD, different authors have evaluated the influence of the experimental parameters on the structure and the morphology of the diamond crystals and films deposited. It is clear that similar deposits were obtained by different methods ranging from spherical rounded shapes to well-crystallised cubes, cubo-octahedrals, octahedrals, single and multi-twinned crystals and polycrystalline layers, which seems to indicate that a general mechanism independent of the deposition method is responsible for the deposit structure. However if the influence of some experimental parameters is clearly established, some discrepancies on the influence of other parameters apparently appear. For example, the temperature dependency of the morphology reported by R. Haubner and B. Lux /13/ is cubes at low temperature and octahedrons at higher temperature on the contrary to the results of B.V. Spitsyn et al. /1/ and some others /14/ who reported a change from an octahedral to a cubic morphology by increasing the temperature.

Our own experimental results from microwave plasma assisted CVD from methane-hydrogen mixtures are reported, but our aim is also to propose here a simplified global approach of the deposition process, without any mechanistic hypotheses on the nature of the hydrocarbon species important for growth, but which allows to represent the influence of the experimental parameters and to deduce some general important characteristics for diamond deposition.

2 - EXPERIMENTAL TECHNIQUES

The reactor consisted of a quartz tube crossing a waveguide structure fitted with two mobile short circuit terminations for impedance matching and connected to a generator which could supply up to 1.2 kW of microwave energy at 2.45 GHz. The reactor was pumped by a 12 m³/h rotary pump and the pressure was measured by a 0-100 torrs absolute pressure gauge. The flow rates of methane and hydrogen were measured and regulated by mass flowmeters and the purity of these gases were respectively of 99.9 % and 99.95 % by volume.

Most of the experiments were carried out on molybdenum samples but silicon and cemented carbides were tested as substrates. The sample temperature was measured by a thermocouple fitted inside the substrate which was set via a quartz support in the waveguide structure. The deposition procedure was quite simple. After evacuation of the reactor at a pressure of 10⁻² torr, a hydrogen flow was established and the discharge initiated in pure hydrogen. When the deposition temperature was reached, CH₄ was introduced. In these experiments, the microwave power was used both to generate the discharge and to heat the sample: therefore the power density and the substrate temperature were in part dependent process parameters.

The morphology and the structure of the deposits were studied by optical and scanning electron microscopy, by X-Ray diffraction and by micro-Raman spectroscopy.

3 - EXPERIMENTAL RESULTS:

3.1 Morphological study:

The most typical morphologies of the deposits on molybdenum are shown on figure 1. Continuous layers or separate crystals were obtained as a function of the deposition conditions and preparation of the surface. The deposit of figure 1a is typical of the poor crystalline quality of microcrystalline spherulites at the beginning of the formation of some bigger faces, deposited in the following conditions: 2% CH₄ in H₂, FT = 100 ml/min (total flux), P = 30 torrs, T = 910°C, P_M = 400 W (microwave power), and t = 2 h.

In conditions not far from these first ones, but for example at higher plasma density, square crystal facets were obtained, in general at high rates of deposition. Figure 1b shows the evolution to the pure square morphology and a fracture of such a 40 μm layer deposited in 8h.

Figure 1c is typical of a surface morphology where the (111) faces are more abundant, here with a great number of twins, which was obtained in the following conditions: 0.5% CH₄ in H₂, FT = 40 ml/min, P = 30 torrs, T = 950°C, P_M = 400 W, and t = 7h. With such low concentration of CH₄, a continuous layer can only be obtained by scratching the surface. With better polished substrates, the nucleation density is much lower and separate crystals as shown on figure 1d, e, f, grow with similar conditions of the experimental parameters. The crystals present generally a cubo-octahedral morphology (fig. 1e) or multiple twins leading to various habits like the pentagonal pseudo-symmetric polycrystal of figure 1f.
Fig. 1: Typical morphologies of the deposits
Fig. 2: - Raman spectra corresponding respectively to the typical morphologies of figure 1 (a) to (d).

Fig. 3: - Raman spectrum recorded on a polycrystalline layer with predominant (111) faces.
3.2 Raman study:

The Raman spectrum of pure diamond exhibits a single sharp peak at 1332.5 cm$^{-1}$, and a polycrystal of graphite shows one line at 1580 cm$^{-1}$. However, microcrystalline graphite and disordered carbons show at least two broad bands, with a displacement of the maxima of the graphite band in the range 1550 - 1610 cm$^{-1}$ probably due to interstitial defects, and a second band at about 1350 - 1380 cm$^{-1}$ due to the in-plane defects /15-21/. An additional third band located around 1500 cm$^{-1}$ and attributed to interstitial defects, either between the graphite layers or between basic structural units, has been reported by J.N. Rouzaud et al. /20/ from the decomposition of Raman spectra recorded on evaporated carbon films after different stages of graphitization.

Figure 2 (a,b,c,d) presents Raman spectra corresponding respectively to the typical morphologies shown on figure 1. It is clear on figure 2a that the spherulitic morphology corresponds to a highly defective deposit with the three broad bands at about 1500, 1500 and 1360 cm$^{-1}$, characteristic of disordered carbons, a fourth band at about 1150 cm$^{-1}$ which has been attributed recently to microcrystalline diamond /22/, and the diamond peak at 1337 cm$^{-1}$ far from the 1332.5 cm$^{-1}$ value of perfect diamond.

Figure 2b presents the spectrum corresponding to the cubic habit of figure 1b which appears also as a poorly organized diamond layer with a broad peak at 1335 cm$^{-1}$. A better result is obtained when (111) faces prevail as shown on figure 2c where only a flat band at about 1520 cm$^{-1}$ subsists. However, the diamond peak is centered at 1335 cm$^{-1}$ and remains broad, more than 10 cm$^{-1}$.

The best results were obtained on single crystals, as shown on figure 2d with a spectrum recorded on a (100) face of a cubo-octahedron. The half-width of the diamond peaks obtained on single crystals is, however, always equal or higher than 5 cm$^{-1}$, but the Raman shift is 1333 cm$^{-1}$. This optimal result was never reached on polycrystalline layers as shown on figure 3 which presents a spectrum recorded on a (111) faceted layer where twinning is minimized.

A detailed study of the spectra recorded in a wider range of conditions is not the object of the present paper and will be reported elsewhere.

3.3 Influence of the experimental parameters:

The morphology and the structural quality of the deposits were studied in a large range of experimental conditions:

CH$_4$ concentration : 0.3 - 3%

total gas pressure : 5 - 40 torrs

total gas flow rate : 20 - 200 ml/min STP

substrate temperature : 750 - 950 °C

microwave power : 300 - 1000 W

reaction time : 2 - 20 h

As shown previously, for example, in the hot-filament method /9/ the influence of the methane concentration is important. Figures 4 and 5 compare for example the morphology and Raman spectra of three deposits obtained from CH$_4$ concentrations respectively of 3, 2 and 0.5 %, the other parameters being maintained constant among which the same surface preparation. It is clear that the nucleation density decreases and the structural quality increases when the methane concentration is lower, leading to one conclusion that nucleation and growth are functions of the relative concentration of some hydrocarbon active species to the concentration of active hydrogen at the gas-solid interface.

The influence of the other experimental parameters is not so simple as they are more coupled with the plasma conditions but it can be concluded that the nucleation density increases at high flux, low pressure and low temperature and the structural quality increases inversely at low flux, high pressure and high temperature (corresponding for this last parameter to high microwave power).

It is interesting to note that different combinations of the experimental parameters can lead to the same morphology and degree of structural order, therefore via similar deposition conditions at the gas-solid interface. Moreover, similar morphology and structure are obtained from the various techniques employed to deposit diamond, increasing the interest to discuss the influence of these interfacial parameters instead of the direct experimental ones.
Fig.4: Influence of the methane concentration on the deposit morphology
($F_T = 25 \text{ ml/mn}, T = 880^\circ\text{C}, P = 15 \text{ torrs})$

a) $\text{CH}_4 = 3\%, t = 2 \text{ h}$; b) $\text{CH}_4 = 2\%, t = 2\text{h}$; c) $\text{CH}_4 = 0.5\%, t = 8\text{h}$.

Fig.5: Raman spectra corresponding respectively to the deposits of figure 4 (a, b, c).

4 - DISCUSSION:

Various studies and discussions have been published concerning the deposition process of diamond either based on global kinetic theories sustained by experimental kinetic information /reviewed in 23/ or which propose elementary reaction mechanism for growth /24, 25/. The discussion is based here on a simplified approach of the deposition conditions at the gas-solid interface, taking into account the conditions of the active species production in the plasma.

In this approach the influence of ions is neglected as ion bombardment leads often to more defective deposits with graphite incorporation as shown in d.c. plasma CVD /5/ but also in our experiments with an independent d.c. substrate biasing in microwave plasmas. On the contrary, positive biasing does not change our own results, d.c. discharge technique is only effective for diamond deposition if the substrate is mounted on the anode /5/, and electron-assisted CVD is a well-known technique, although a great number of experiments are carried out at floating potential and the important fact may be a limited ion bombardment rather than an enhancement by electrons.

Then the deposition process is decomposed in the production of active neutral species in the discharge and their interaction with the solid surface. In a simplified model, the active species considered are some $\text{CH}_x$ neutrals (radicals or molecules), and hydrogen atoms whose
importance is indicated in a number of papers to remove graphite preferentially to diamond, to stabilize sp$^2$ bonding or (and) to decompose hydrocarbon radicals.

It is not our purpose to discuss all the possible reactions responsible for formation and loss of these species. Then the principal elementary reactions considered, with their rates $R_i$, are for CH$_4$-H$_2$ mixtures:

I) - Hydrogen dissociation by electron impact:

\[ H_2 + e^- \xrightarrow{k_1} 2H + e^- \quad R_1 = k_1 |e^-| |H_2| \]

II) - Methane dissociation by electron impact which is for the first radical production:

\[ CH_4 + e^- \xrightarrow{k_2} CH_3 + H + e^- \quad R_2 = k_2 |e^-| |CH_4| \]

and more generally leads to CH$_n$ radicals. These above dissociation rates are functions of the electron density, the electron energy distribution function and the dissociation cross-sections of the different species. In the same manner, ion production by electron impact could be considered but their interaction with the solid surface will be neglected, as discussed below.

III) - Then a great number of radical reactions could be considered in the plasma. Among them we may consider the dehydrogenation by atomic hydrogen, the first example being:

\[ CH_4 + H \xrightarrow{k_3} CH_3 + H_2 \quad R_3 = k_3 |H| |CH_4| \]

and more generally which leads also to CH$_n$ radicals. Other reactions which lead to various stable hydrocarbon species could also be considered like the formation of C$_2$H$_2$, which was the basis of the elementary mechanism proposed by M. Frenklach and K.E. Spear /25/.

However the interaction of all these species generated in the plasma with the surface can be summarized as a possible deposition from some CH$_x$ neutrals and etching by atomic hydrogen. These reactions at the surface can be written for diamond ($d$) and graphite ($g$) as a general single reaction for deposition and etching:

IV) - Deposition from CH$_x$ and etching by hydrogen atoms:

\[ CH_x \xrightarrow{k_d, k_g} ^<C^> + x H \quad R_d = k_d |CH_x| |H| \quad R_{d'} = k_{d'} |H|^r \]
\[ CH_x \xrightarrow{k_g, k_g} ^<C^> + x H \quad R_g = k_g |CH_x| |H| \quad R_{g'} = k_{g'} |H|^v \]

without any hypothesis on the order of the different reactions. Thus, two stages shall be considered as function of time, the nucleation and the growth ones.

4.1 Nucleation:

The classical theory of homogeneous nucleation points out the relative contributions of volume and surface energies in the free energy of formation of a nucleus which allow to define the critical size of a nucleus at which it may lower its free energy whether it grows or shrinks. This theory of homogeneous nucleation also brings out the importance of the supersaturation, as the vapour must be supersaturated for small clusters to have any stability, and as the critical size decreases when the supersaturation increases leading to higher rate of nucleation.

Nucleation on a substrate presents new features as small clusters gain some degree of stability because of bonds with the substrate and the critical nucleus size is much smaller than for nucleation within the vapour. Atomic theories of nucleation (for example reviewed by Frankl and Venables /26/) are used to predict the critical nucleus size, the rate of nucleation, saturation density of stable clusters and the variations of these with supersaturation and temperature. However no detailed experimental comparison with theory is possible except in a few cases /26/ and defects in the substrate (grain boundaries, dislocations...) or impurities seem to play an important role. Thus the effect of supersaturation, state of the surface and possible contribution of impurities will be discussed successively.

Let us consider the single overall reaction IV for deposition and etching respectively of
diamond and graphite, and a hypothetical equilibrium reaction between gaseous carbon and the important gaseous active species within the gaseous phase supersaturated with respect to the solid at the gas-solid interface:

\[
\text{CH}_x \rightleftharpoons C + xH
\]

with the equilibrium constant \( K = |C| |H|^x / |CH_x| \)

For given concentration of \( H \) and \( CH_x \) and a given temperature the actual carbon gaseous concentration at the interface can be approximated by \( |C| = K |CH_x| / |H|^x \)

At equilibrium between the gaseous phase and the solid, the equilibrium gaseous concentration becomes \( C_0 \):

\[
<C> \rightleftharpoons C \quad K_0 = |C_0| = e^{-\Delta G_0 / RT}
\]

According to the relative free energy of formation of diamond and graphite (\( \Delta G_f, C_d > \Delta G_f, C_g \)), the equilibrium constants over diamond and graphite are such that \( K_{o,d} > K_{o,g} \).

Out of equilibrium between the gas phase and the solid, the supersaturation over the solid is defined as \( \Sigma G = |C| / |C_0| \) and is about two times higher over graphite than over diamond. It is interesting to note that these supersaturations can be here expressed at a given temperature only by the ratio between \( |CH_x| \) and \( |H|^x \) concentrations at the gas-solid interface:

\[
\Sigma_{C_d} = \frac{K |CH_x|}{K_{o,d} |H|^x} \quad \Sigma_{C_g} = \frac{K |CH_x|}{K_{o,g} |H|^x}
\]

Thus, it is clear that the nucleation process can be in part controlled by the experimental parameters which set the temperature and the interfacial gaseous concentrations, in such a way that the nucleation of the stable graphite phase will be limited, at sufficiently low supersaturation. At this quite modest supersaturations, the critical nucleus may contain a few atoms and the influences of the substrate and impurities become important.

Derjaguin and Fedoseev have shown by calculation, that the nucleation rate of diamond exceeds the nucleation rate of graphite on (111) surface of diamond, in some range of low supersaturations /27/. The nucleation on non-diamond substrates is greatly affected by their nature as reviewed recently by A.R. Badzian et al. /28/. Moreover, it is well-known that the surface preparation plays an important role and that a sufficient nucleation rate is, at the low supersaturation employed, achieved only by creating appropriate defects, except at high concentrations of the reactive species reached in high power density methods /5,6/ where the nucleation conditions seem to be changed by the high "exchange current", that is the high reverse etching reaction which can be reached. In any case one cannot ascertain if the mechanism of diamond nucleation always require some impurities like Si or some metals, often carbide forming elements /28, 29/.

4.2 Growth:

It is well known that diamond can grow on graphite and that graphite can be obtained on diamond. The deposit structure depends on the deposition conditions at the gas-solid interface which are function of the gaseous concentrations and surface temperature. As for the nucleation stage, these conditions will be examined by considering the overall reaction IV of deposition and etching and the relative rates for diamond and graphite. The net deposition rates for diamond and graphite are respectively:

\[
R_{d,\text{net}} = k_d |CH_x|^q - k_d' |H|^r \quad R_{g,\text{net}} = k_g |CH_x|^u - k_g' |H|^v
\]

To avoid the growth of graphite, \( R_{g,\text{net}} \) must be at least equal to 0, that is to say:

\[
|CH_x|^u / |H|^v \leqslant k_g' / k_g
\]

When the concentration of \( H \) increases, the concentration of \( CH_x \) can be increased accordingly without deposition of graphite. At the limit where \( R_{g,\text{net}} = 0 \) the expression of \( |H| \) can be calculated and substituted in the expression of the net deposition rate of diamond.

\[
R_{d,\text{net}} = k_d |CH_x|^q - k_d' (k_g' / k_g)^r / |CH_x|^u/v
\]

or

\[
R_{d,\text{net}} = k_d' (k_g / k_g')^r / |CH_x|^u/v ((k_d / k_d') (k_g' / k_g)^r / |CH_x|^u/v - 1)
\]
When the graphite growth is just suppressed, a positive growth rate of diamond will exist if
the difference in the brackets remains positive for the actual kinetics constants and reaction
orders.

This possibility is effectively observed experimentally and can be correlated to the various
experimental results which have shown that the etching rate of graphite by hydrogen atoms is
more than one order of magnitude greater than the etching rate of diamond
\( k'_d|H|^{r} \ll k'_g|H|^{v} \), if the deposition rates are furthermore of the same order.

Therefore, if the concentration of hydrogen atoms is moderate, the \( CH_x \) concentration must be
low to deposit pure diamond and the deposition rate of this pure diamond will be low as shown
by \( \text{R}_{\text{net}} = f[CH_x] \), and represented schematically on figure 6a. To further increase the
deposition rate of pure diamond, two possibilities exist:

- by maintaining \( \text{R}_{\text{net}} < 0 \) with a sufficiently low \( |CH_x|^{U}/|H|^{V} \) ratio but increasing
simultaneously the individual values of the \( CH_x \) concentrations and H concentration and by
increasing the "exchange current" of reactions IV for diamond and graphite, that is the
etching rates, but also \( \text{R}_{\text{net}} \) for particular combinations of the reaction orders, for example
if they are all equal to 1. In that case a higher deposition rate of diamond which preserved
its purity can be represented schematically as on figure 6b, where a higher power density in the
plasma can be coupled with higher hydrocarbon concentration and total pressure, eventual-
ly also with a higher total flow rate.

Fig.6 : - Schematic influence of the plasma density, total pressure and \( CH_4 \) concentration on
the deposition and etching rates of graphite and diamond.

Diamond without many defects can effectively be deposited at high rates, at higher pressure
and hydrocarbon concentration, if the power density is very high as shown in DC-discharge
plasma CVD at high voltage /5/ and also in thermal RF-plasma CVD /6/.

- by changing the chemistry of the process to increase "the exchange current" of the
reaction of type IV. This can be done by the introduction of O atoms in the system at higher
pressure, apparently whatever the nature of the O-containing feed molecule (\( CH_3OH \), \( CH_3COCH_3 \),
\( H_2O \), \( O_2 \)...) as shown by various authors /29, 30/.

Finally, concerning the special case of deposition from \( CH_4 - H_2 \) mixtures and, even if it
cannot be totally excluded, different hydrocarbon species that might favour one or the other
carbon structure, the previous general discussion on the nucleation and growth stages shows
the primary influence of the hydrocarbon concentrations at the gas-solid interface relative
to the atomic hydrogen one. The interfacial \( CH_x \) concentration is influenced by the \( CH_4 \) inlet
concentration, the total flux and the total pressure but also by the plasma density and the
electron energy distribution function, and also by the gas temperature. The atomic hydrogen
concentration at the interface is principally a function of the power density and total pres-
sure and, to a lesser extent, a function of the \( H_2 \) inlet concentration and the total flux.

The interfacial parameters include the surface temperature in addition to the gaseous concen-
trations \( |CH_x| \) and \( |H| \). The influence of this third parameter on the adatom mobility is well-
known but it also influences somewhat the supersaturation at the gas-solid interface by
changing at once the thermodynamics and the kinetics. Our results and other published ones
/3/ show that the nucleation density of diamond decreases with the temperature, certainly as a result of the difference in mobility at the substrate surface rather than in supersaturation. Concerning the final purity of diamond, it appears that the temperature is less important than the interfacial concentrations.

4.3 Deposit morphology and structure:

In addition to the degree of structural order of the diamond deposits or amount of sp² bonds incorporated, the above interfacial parameters control the morphology of the deposits, taking into account the relative stability of the principal diamond faces.

A number of different authors have reported the different crystal habits which can be obtained, ranging from spherulitic polycrystalline shapes and irregular forms to well-faceted separate crystals with cubic, cubo-octahedral or octahedral habits showing eventually single and multiple (111) twins, and to polycrystalline layers composed of the preceding forms. All these habits have been obtained by different deposition techniques, the best known being the hot-filament and microwave plasma ones, indicating a similar mechanism at the gas-solid interface. However some apparent discrepancies appear between these results upon the influence of the external experimental parameters on the morphology. As indicated previously, B.V. Spitsyn et al. for example reported a change from an octahedral to a cubic morphology as the deposition temperature increases /1/; R. Haubner and B. Lux showed an opposite effect of the temperature with cubic shaped crystals at low substrate temperatures and more and more octahedral crystals at higher temperatures /13/.

This example among others indicate that different combinations of the externally controlled experimental parameters can lead to similar deposition conditions and that the morphology changes should also be discussed as a function of the interfacial deposition conditions. The crystal habits are also determined by their relative stability. From the surface energy calculated by Vyatkin /31/, it can be shown that the octahedral shape is the thermodynamically most stable diamond habit followed by the cubo-octahedral and then the cubic one.

![Diagram](image)

Fig.7: - Schematic influence, between about 750 and 950°C, of the interfacial parameters on the deposits morphologies and structures (□ = graphite ; △ = microcrystalline spherulites ; (100) faceted layer ; (111) faceted layer ; — = etching).

These different morphologies together with the spherulitic rounded shapes and graphitic deposits occur for specific deposition conditions at the gas-solid interface as shown schematically on figure 7 where the interfacial parameters are the concentrations in hydrocarbons.
and hydrogen atoms, and the temperature in the range 750 - 950°C. This diagram were constructed from some published results and our own experimental results taking into account the qualitative influence of the external experimental parameters on the interfacial concentrations and sometimes the coupled character of some parameters, for example temperature and power dissipated in the plasma in microwave plasma reactors without external heating.

This diagram presents some characteristics features:

- The influence of temperature is less important than the influence of the interfacial concentrations.

- The graphitic structure can develop at high concentration in CH\(_x\) and low concentration in hydrogen atoms and the contrary for diamond.

- The most stable octahedral morphology of diamond is obtained at low supersaturation in CH\(_x\) and high concentration of hydrogen. It may be noted that only the cubo-octahedral form is generally reached in cold-wall microwave plasma, even at high plasma density on the contrary to hot-wall reactor /13/, leading to the conclusion that the concentration in active CH\(_x\) species depends also of the degree of advancement of the reactions between the neutral species in addition to the influence of the classical parameters.

- The less stable cubic morphology is deposited when kinetically favoured, at higher CH\(_x\) concentrations. These deposits are consequently more defective as shown by Raman spectroscopy. Some (100) faces can besides grow on the spherulitic rounded shapes which contains both disordered graphitic and diamond structure.

- The different morphologies can all be obtained in a large range of temperature depending on the combination with the other interfacial parameters.

These interfacial deposition conditions influence the nucleation density. In addition, the surface preparation plays an important role. These above morphologies can be deposited either as separate crystals or in the form of a polycrystalline layer, with a high nucleation density of the most stable form being however more difficult to obtain at moderate power densities, as expected at the low [CH\(_x\)] concentrations necessarily employed. Figures 8a and 8b shows two polycrystalline layers with, respectively, a cubic morphology and predominant (111) faces.

Fig.8 : - Polycrystalline layers with : a) a cubic morphology and b) predominant (111) faces.

- Finally, heteroepitaxial growth of diamond in the \langle111\rangle direction should be searched in conditions of high "exchange current" and low deposition rate, that is to say high partial pressures of hydrogen atoms associated with low concentrations in CH\(_x\).
5 - CONCLUSION

A detailed understanding of the diamond deposition process is not well established but a qualitative discussion of the interfacial deposition conditions instead of a direct examination of the influence of the external experimental parameters was tried to deduce some general characteristics concerning:

- the control of the morphology and the structural quality of the deposits,
- the influence of the deposition methods reduced to their ability to produce low or high concentration of the active species, especially H atoms.

It is clear that in-situ diagnostics of the gaseous phase coupled to the determination of the plasma parameters would provide essential information in this domain.

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