

Substrate Position Influence in the DC Plasma Jet Chemical Vapour Deposition of Diamond

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The influence of the substrate position in the different regions of the plasma jet was examined depending on the morphology, deposition rate, surface area of the deposited diamond films and their phase purity while other parameters of the process were kept constant (CH_4/H_2 ratio, plasma power, chamber pressure and substrate temperature). An increase in the substrate distance from the anode nozzle opening of the torch leads to a considerable change in morphology (from a perfect crystallinity to a ball-like structure), as well as to a decrease in deposition rate and an increase in the coated surface area. According to XRD findings, the phase purity of the deposits does not deteriorate significantly, so it can be described as a diamond coating in the entire region studied. A reason could be the enthalpy of plasma gases high enough to preserve a relatively high concentration of atomic hydrogen which is known as a good etchant for non-diamond carbon phases.

Key words: diamond, chemical vapour deposition, plasma jet.

Introduction

EXISTING methods for industrial diamond synthesis demand high pressure (50-100 kbar) and high temperature (about 2500K), while a produced diamond is in a fine-ground powder form (industrial diamonds). Diamond coatings could be obtained using the chemical vapor deposition (CVD) in the P-T range of diamond metastability (pressures below 1 bar and a temperature of 1000K) [1]. Important industrial materials can be coated with diamonds in order to improve some characteristics: tribological, electro thermal, corrosive, etc. Therefore, diamond coatings have wide industrial application: in medicine (hip implants), in mechanical industry (coated carbide inserts), in electronics (substrates for electronics devices, different sensors), and for military purposes (windows for high power microwave sources) [2].

There are four basic techniques of thermal excitation of the starting hydrocarbon gas by the decomposition of which it is possible to obtain CVD diamond. These techniques are generated by the microwave thermal plasma methods, or by radio frequency discharges, as well as thermal plasma obtained by passing DC currents (especially in the DC plasma jet technique), hot filament techniques and techniques using flame [3]. Due to a high plasma temperature of 10-20 000 K, the method of DC plasma jet is known as the method that gives a diamond deposit of the highest phase purity with the largest linear growth of deposit ($\mu\text{m/h}$) [4, 5].

The least studied parameter of all deposition parameters in the process of CVD diamond synthesis (nature of substrate, chamber pressure, substrate temperature, composition of gas) is the position of substrate in plasma. The position of substrate is an important parameter in the CVD process as it is shown that there is a concentration

dependence on the radicals in the $\text{Ar}/\text{H}_2/\text{CH}_4$ plasma from the axial downstream position in the plasma jet [6]. In the works dedicated to the problem of substrate position [4, 7, 8] in the DC plasma jet diamond synthesis, the authors faced the problem of difficult temperature control of substrate positioned in the different areas of the plasma jet due to differences in the thermal flux. Concerning this fact, our aim was to investigate the nature of deposits in the different zones of the plasma jet with strict maintenance of a constant substrate temperature. We were engaged in the deposition of diamond layers in the DC $\text{Ar}/\text{H}_2/\text{CH}_4$ plasma jet. Distinctly colored zones in plasma were identified. The methods of optical microscopy and X-ray diffraction (XRD) were applied to evaluate the quality of synthesized diamond as a function of substrate position when other processing parameters were kept constant.

Methods

The deposition was carried out in an apparatus consisting of a plasma torch mounted on the top of a water-cooled vacuum chamber and a water-cooled substrate holder to which the substrate was attached [9]. The deposition parameters are given in Table 1.

Table 1. Basic deposition parameters

| | |
|---------------------------|-------------|
| Voltage (V) | 25.3 - 26.0 |
| Current (A) | 92 - 94 |
| P (kW) | 2.4 |
| Ar (L/min) | 7.4 |
| H_2 (L/min) | 2.2 |
| CH_4 (L/min) | 0.04 - 0.06 |
| Chamber pressure (mbar) | 250 - 280 |
| Substrate temperature (K) | 1300 - 1320 |

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The morphology of deposits was investigated by a Scanning Electron Microscope (SEM) JEOL JSM-35. Crystallographic studies were performed applying the X-ray diffraction (XRD) analysis using a Siemens Kristalloflex-4 apparatus with CuK α 1 radiation (0.154051 nm). Molybdenum plates with dimensions 20x20x1mm³ were used as a substrate. They were previously mirror-like polished with corundum (Al₂O₃) sand paper and then washed in the ultrasound bath. The substrate temperature was measured with a Chromel Alumel thermocouple placed below the substrate.

Results and discussion

Three colored regions can be clearly distinguished in the structure of the Ar/H₂/CH₄ plasma jet, Fig.1. A zone of white plasma (with strong atomic and ionic lines of argon) extends just behind the anode hole, then a purple plasma zone (due to the emission of atomic hydrogen) appears, and, finally, a long tail of green plasma (emission of C₂ radicals, Swan system). The deposition of three regions (A, B, C) was examined, as indicated in Fig.1. The total investigated range throughout all zones extends to about 40 mm along the plasma.

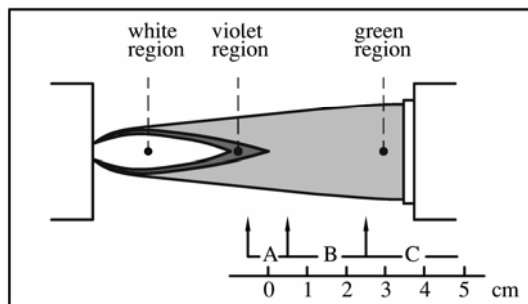


Figure 1. Characteristic regions suitable for diamonds deposition (A, B, C)

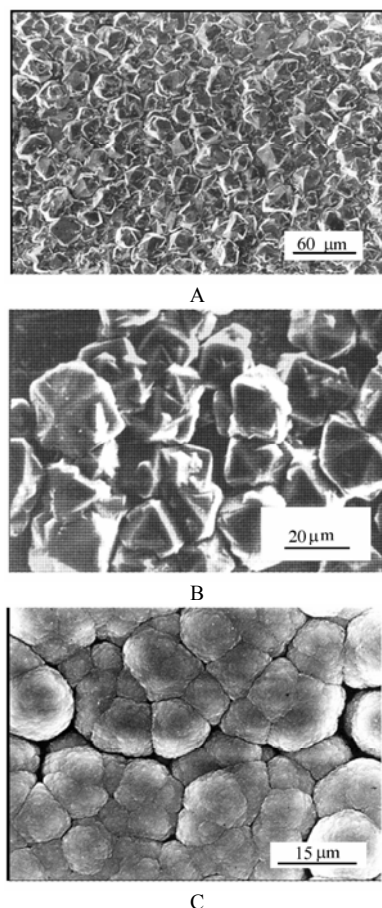


Figure 2. Morphology of diamond deposit in the zones A, B and C

A typical appearance of deposits in three areas studied is shown in Fig.2. The deposits in the zone A (the time of deposition was 5 min) and in the zone B (the time of deposition was 15 min) exhibit the cubic-octahedral morphology. The deposit in the zone C (the time of deposition was 60 min) possesses a ball-like structure. The colors of deposit change from transparent-gray (zone A) and gray (zone B) to black in the area C. The plasma jet conically spreads from the anode nozzle opening and thus the surface area of the deposited zone increases going from the zone A to the zone C. Therefore, the estimated area of deposits in Table 2 is given together with an estimated growth rate of crystals as derived from the crystal size and time of deposition.

High speed of deposition in the zone A results in a very low nucleation density on the surface of the substrate because nuclei develop into crystals very quickly. Due to this fact, diamond layers developed in this way can spontaneously detach from the surface at the time when residual stresses overcome the adhesion force as a consequence of coating cooling. Also, the increment of deposited mass decreases three times going from the zone A to the zone C which may be concluded from the product of surface deposit and the linear crystal growth rate given in Table 2.

Table 2. Surface areas of the deposit and the linear crystal growth rate in the zones

| Deposition zones | A | B | C |
|------------------------------------|---------|-------|------|
| Area of deposit (cm ²) | 0.2 | 0.8 | 2.5 |
| Linear crystal growth rate (μm/h) | 300-500 | 60-80 | 7-10 |

All deposited layers showed clearly defined XRD diamond reflections. Table 3 summarizes the experimentally determined values of the interplanar distance (d_{hkl}) of the corresponding (hkl) diamond reflections and the corresponding intensity I/I_0 reflection relationship given for the deposits in the zones A, B and C, calculated as mean values from the 3-5 XRD patterns available inside each group. At the same time, the literature and the standard values (d_{hkl} , I/I_0) for natural polycrystalline diamonds are given in Table 3

Table 3. d_{hkl} and I/I_0 for the deposits in zones A, B and C and for natural diamonds

| (hkl) | Zone A | | Zone B | | Zone C | | Natural diamond | |
|-----------|----------|---------|----------|---------|----------|---------|-----------------|--------------|
| | d (nm) | I/I_0 | d (nm) | I/I_0 | d (nm) | I/I_0 | d_{ref} (nm) | I/I_{0ref} |
| 111 | 0.2053 | 100 | 0.2056 | 100 | 0.2053 | 100 | 0.2052 | 100 |
| 220 | 0.1267 | 18 | 0.1264 | 44 | 0.1266 | 43 | 0.1265 | 25 |
| 311 | 0.1076 | 12 | 0.1076 | 22 | 0.1076 | 20 | 0.1076 | 16 |

Table 4 shows the intervals of the values corresponding to the pure diffraction line broadening ($\beta_{1/2}$), and the values of the crystallite size (L_c) and the lattice constants (a) calculated according to the most intensive reflection line (111).

Table 4. Values of $[\beta_{1/2}, L_c, a]_{111}$ for the deposits in A, B and C regions of plasma jet

| Regions | $\beta_{1/2}$ (2 θ°) | L_c (nm) | a (nm) |
|---------|-----------------------------------|------------|---------------|
| A | 0.100-0.107 | 82-84 | 0.3554-0.3557 |
| B | 0.082-0.159 | 63-103 | 0.3561-0.3568 |
| C | 0.091-0.124 | 74-89 | 0.3554-0.3559 |

Data from Tables 3 and 4 show that the deposit in all three zones is polycrystalline diamond with a somewhat higher (110) preferential orientation of the zones B and C. The crystallite size and lattice constant parameters are practically the same in the whole range of distance

deposition. From the aspect of morphology and the linear crystal growth rate, the substrate position in the plasma is the most critical parameter, with the other parameters of deposition being kept constant. However, in terms of deposit quality, bearing in mind the phase purity, it is a factor of less importance, judging by the XRD results.

In the papers [4, 7, 8] the authors applied very similar deposition parameters, even a plasmatron with similar power, about 3 kW, was used. They also identified three morphologies, two of which are of a polyedric and spherical form (similar to our C deposit) which, according to these authors, occurred only when the relation CH_4/H_2 was higher than 8%. In this case, the deposit does not show any XRD reflections, and does not match the quality of our "spherical" deposit. The authors have used significantly higher flow of argon as the main plasma gas, i.e. 20 L/min, which was about three times higher than in our case (7.4 L/min). Therefore, the enthalpy of their plasma was significantly lower. According to these facts, it was expected [6, 10] that the concentration of atomic hydrogen, responsible for non-diamond phase etching, would be higher along the plasma jet we used. This is probably the reason why our ball-like deposit is essentially the phase-pure nanocrystalline diamond. Its black color indicates the possible presence of graphite phase, and the Raman spectroscopy, due to its much greater sensitivity to the graphite phase, would give a better insight into the quality of this material.

Conclusion

The substrate position in the DC plasma jet method for diamond deposition applying the CVD technique proved to be decisive from the standpoint of deposit morphology, linear crystal growth rate and the area of deposit on the substrate. Thus, at a distance of 40 mm along the plasma,

going in the direction of plasma outflow, the linear crystal growth rate decreases 50 times, whereas the deposit area increases 10-12 times. Although the deposit morphology changes along the plasma path from a well crystalline to a ball-like, the XRD methods of characterization confirmed that all deposits are a phase-pure diamond. All deposits are composed of crystallites of 70-100 nm, regardless the investigated range of the deposition distance. The values of the calculated interplanar distance constant and the lattice constants of all studied deposits are consistent with the tabular values for natural diamond.

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Uticaj položaja substrata u procesu deponovanja dijamenta iz parne faze u metodi jednosmernog lučnog plazmenog mlaza

Ispitivan je uticaj pozicije substrata na morfologiju, brzinu deponovanja, površinu deponovanih dijamantskih filmova i na njihovu faznu čistoću, pri čemu su svi ostali parametri procesa (odnos CH_4/H_2 , snaga u plazmi, pritisak u komori i temperatura substrata) držani konstantnim. Sa povećanjem distance nanošenja od anodnog otvora plazmatrona dolazi do značajne promene u morfologiji depozita (od kristalne do loptaste), do smanjenja brzine deponovanja i povećanja površine pokrivenosti depozitom. Rezultati difrakcije X- zraka (XRD) ukazuju na to da su svi depoziti fazno čist dijamant. Razlog za fazno čist dijamant može biti u visokoj entalpiji korišćene plazme, čime se održava relativno visoka koncentracija atomskog vodonika, koji je zbog svoje reaktivnosti efikasan u procesu nagrizanja ne-dijamantskih faza.

Ključne reči: dijamant, hemijsko-parna depozicija, mlaz plazme.

Влияние положения подложки в процессе депонирования алмазов из паровой фазы в методе однонаправленной сводчатой струи плазмы

Здесь испытывалось влияние положения подложки на морфологию, на скорость депонирования, на поверхность депонированных алмазных фильмов и на их фазовую чистоту, причём все остальные параметры процесса (отношение CH_4/H_2 , сила в плазме, давление в камере и температура подложки) задерживались постоянными. С увеличением расстояния нанесения от анодного отверстия плазматрона происходят значительные изменения в морфологии депозита (от хрустальной до шариковой), до снижения скорости депонирования и до

увеличения поверхности покрытия депозитом. Результаты дифракции X-лучей (XRD) указывают на то, что все депозиты являются фазовым чистым алмазом. Причиной фазового чистого алмаза может явиться высокая энтальпия использованной плазмы, чем сохраняется относительно высокая концентрация атомарного водорода, который из-за своей реактивности является эффективным в процессе разъедания не-алмазных фаз.

Кljučne riječi: алмаз, химико-паровое депонирование, струя плазмы..

Influence de la position du substrat dans le processus de la déposition du diamant de la phase vapeur dans la méthode du jet de plasma

On a étudié l'influence de la position du substrat sur la morphologie, la vitesse de déposition, la surface des films de diamant déposés et aussi sur leur pureté de phase alors que tous les autres paramètres du processus (le rapport CH₄/H₂, la force du plasma, la pression dans la chambre et la température du substrat) étaient constants. Avec l'augmentation de la distance de déposition à partir de l'ouverture d'anode plasmatron un changement important se produit dans la morphologie du dépôt (de cristalline jusqu'à la forme de balle) la vitesse de déposition diminue et la surface couverte de dépôt augmente. Les résultats de la diffraction des rayons X (XRD) démontrent que tous les dépôts représentent le diamant de phase pur. L'explication pour le diamant de phase pur peut se trouver dans la grande enthalpie du plasma utilisé ce qui démontre une grande concentration de l'oxygène atomique qui est très efficace à cause de sa réactivité dans l'action de l'eau forte des phases non diamants.

Mots clés: diamant, déposition chimique de vapeur, jet de plasma.