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Nanocarbon colloid produced by electro-spark discharge in ethanol for seeding the substrates in MPACVD synthesis of polycrystalline diamond films

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Abstract. We produced a nanocarbon colloid by electro-spark discharge as substrate seeding for microwave plasma-assisted chemical vapor deposition (MPACVD) synthesis of micro- and nano-crystalline diamond films and solid free-standing microcrystalline diamond plates. The colloid was produced by a specially designed device via a pulse electro-spark discharge in ethanol. The nanocrystalline diamond films and polycrystalline plates that were grown were examined by optical, SEM and TEM microscopies and Raman spectroscopy.

1. Background
The chemical vapor deposition (CVD) synthesis of diamond at low pressures under metastable conditions [1] has been described in detail in reviews by R.C. De Vries [2] and J.C. Angus [3]. In particular, Angus noted that the phenomenon of diamond nucleation is "much less well understood than the extension of an existing diamond lattice". CVD diamond nucleation has a critical impact on the properties of diamond films, such as their morphology, homogeneity, formation of defects, and adhesion to relevant substrates [4].

Waite and Shah [5] showed via X-ray photoelectron spectroscopy (XPS) that diamond nucleation on non-diamond substrates primarily occurs at the intermediate layer of diamond-like amorphous carbon, on silicon or metal carbides, or on graphite, which are formed during the incubation period due to chemical interactions of the activated gas species with the substrate surface. Initially, silicon carbide (SiC) forms. Then, the surface is oversaturated by carbon; and graphite begins to grow. Singh [6] employed high-resolution transmission electron microscopy (HRTEM) to study the nucleation and subsequent growth of nanocrystalline diamond on copper TEM grids during the process of hot-filament chemical vapor deposition (HFCVD). He presented direct evidence for the formation of diamond nano-crystallites (with a grain diameter of 2–5 nm) covered by a diamond-like amorphous carbon layer with a thickness of 8–14 nm. These diamond nano-crystallites appeared due to the direct transformation of the diamond-like carbon into diamond. The diamond nano-crystallites
in the amorphous carbon layer are assumed to become nucleation sites on which columnar diamond crystallites can grow. The spontaneous nucleation of diamond on foreign (silicon) substrates during the CVD process is generally characterized by a low nuclear density of $\sim 10^4 \text{cm}^{-2}$. The nucleation site density should be many orders higher to obtain thin homogeneous and continuous films. Therefore, before the beginning of the CVD process, additional seeding of the diamond should be performed.

Ultrasonic treatment of a substrate in a suspension of detonation nanodiamond (DND) powder in water or organic liquids is currently the most common method of diamond seeding. Substrate seeding from a solution with a fine fraction of DND powder gives a higher density of nucleation ($>10^{11} \text{cm}^{-2}$) and better uniformity [7, 8]. To increase the nucleation density and growth rate of the diamond films, biasing of the substrate potential is often done [9]. Typically, a DND powder for seeding has a wide dispersion of particle sizes from a few nm to 1 $\mu$m. The diamond powder is composed of primary particles that are 4–5 nm in diameter that combine into cluster structures with sizes of 30–40 nm, and these are then included into larger aggregates on the order of hundreds of nanometers. Nanocrystalline diamond seeding is especially important for the growth of ultra-NCD films that are destined for tribological applications and microelectromechanical systems (MEMS) [8]. The grains in the UNCD films can be less than 10 nm. Therefore, the best grains for seeding should be approximately 2–5 nm in diameter. Therefore, extraction of primary particles from the aggregates is performed via sophisticated fractionation and mechanical grinding in micro-balls mills [10]. Such a nanodiamond colloid has been applied to various substrates and, as a result, a very high diamond seeding density has been obtained [11, 12]. Because the separation of the nanosized diamond fraction has certain technological difficulties that can be overcome only under factory conditions, the powder is usually purchased in the market.

It is important to determine other more affordable means for fine substrate seeding for the CVD synthesis of diamond nanocrystalline films. An example of this type of substrate seeding [13] is the preliminary deposition on a substrate of a thin layer of polyhydrocarbon (PHC) or polynaphthalene hydrocarbon (PNHC) followed by annealing. In the resulting polymer layer, a structure enriched with tetrahedrally coordinated sp$^3$ carbon bonds forms, which act as a precursor in the CVD synthesis of diamond films.

The goal of this study was to determine another method of substrate seeding from a nanocarbon colloid created without DND powder by using electric spark discharge (ESD) in an organic liquid (ethanol) [15, 16]. The use of this colloid for seeding substrates for MPACVD growth of micro- and nano-structural polycrystalline diamond films was quite successful. This paper focuses on the study of silicon substrates seeded with nanocarbon particles in ethanol and the nucleation and growth of microcrystalline and NCD films.

2. Preparation of the nanocarbon colloid by ESD in ethanol
Currently, there is considerable interest in the formation of carbon nanoparticles in organic liquids using ESD systems in which discharges destroy the molecules of organic liquids with subsequent quenching and cooling of the decomposition products, which results in carbon in a nanoscale condensed phase. The ESD systems used to produce nanoparticles in liquids are conventionally divided into two groups with respect to the discharge energy in the pulse: $\sim 1 \text{kJ}$ and $\sim 1 \text{J}$. The first type of system is distinguished by a powerful pulse energy and high loads [17]. In the second type of system, chemical decomposition of liquid molecules occurs in electrospark microchannels, and these are simpler [15, 16]. Therefore, the second system is more relevant to the problem of nanocarbon colloid preparation in a laboratory.

Figure 1 shows a schematic in which the colloid is prepared according to ref. [15]. The multi-electrode system (1) assembled on the dielectric body 2) is immersed into a 0.2 L sink (3) filled with 95% ethanol. Argon is passed through the gaps between the electrodes (4).
Figure 1. Schematic of the ESD device for colloid fabrication: multi-electrode system (1); dielectric body (2); 0.2 L sink filled with 95% ethanol (3); electro-spark channels (4) inside inter-electrode gaps (5) which are blown through with argon.

Parameters for the pulsed source of electrical discharge supply are as follows: voltage of $U \leq 20$ kV, current of $I \leq 300$ A, pulse repetition frequency of $f \leq 50$ Hz, storage capacitor energy of $W \leq 1.6$ J, and an Ar gas flow rate of $V = 1–2$ slm (standard liter per minute) [15, 16]. The formation of a colloid occurs under the following conditions. During electric breakdown in ethanol, spark channels form in gas bubbles of argon saturated with ethanol vapor. In channels with a diameter of $\sim 100$ µm, the gas temperature reaches values of $T_g \sim 4000–5000$ K. The electron temperature, $T_e$, is $\sim 1.5$ eV, and the electron density is $n_e \sim 10^{17}$ cm$^{-3}$. The dissociation and ionization of molecules in the pulsed discharge channels in ethanol creates free atoms and carbon radicals, and as a result of rapid quenching, a condensed phase of nano-sized carbon appears in ethanol. The stability of the obtained colloid depends on a threshold value of specific energy density for the discharge in ethanol of $E \approx 10^{-15}$ J/cm$^3$, depending on the material of the electrode (titanium, stainless steel or copper). The lowest value corresponds to titanium.

3. Characteristics of the ESD colloid

First, the colloid stability was determined from observations via precipitation absence for more than a year. The stability of the colloid might be disturbed only by any external action, such as passing current through the colloid via electrophoresis, by an intense laser or ultrasonic irradiation. Heating the colloid to a temperature close to its boiling point followed by cooling does not affect the stability of the colloid. The nanocarbon colloid stability and particle size distribution were studied by dynamic light scattering (DLS) using a Zetasizer Nano ZS analyzer (Malvern Pananalytical, UK). The $\zeta$-potential is a measure of the magnitude of the Coulomb interaction between nanoparticles and is used as one of the main parameters to assess the stability of a colloid. The measured average value of the $\zeta$-potential of $+32.3$ mV indicates a good degree of colloid stability. The distribution of colloidal particles by their volume can be divided into 3 groups with their maximum values in each group: 34.73 nm (81.6%), 74.41 nm (14.4%) and 789.2 (4.1%).

To analyze the chemical composition of the solid phase of the colloid, it was determined by evaporation of the solvent from the colloid. Figure 2 shows SEM images of dried up colloidal film.
obtained with a Carl Zeiss NVision 40 scanning electron microscope (SEM) at two different magnification values. Nanoscale particles of 30–100 nm and their agglomerates were observed.

The condensed phase of the colloid was studied via a JEM-2100 transmission electron microscope and a JED-2300 energy dispersive X-ray spectrometer. Figure 3 shows the characteristic X-ray spectra of elements and the electron diffraction pattern of the dried up residue of the colloidal drop on the copper TEM grid.

According to the spectrum shown in Figure 3b, in addition to the basic carbon and oxygen atom contents, the colloid contains metal nanoparticles of iron due to sputtering ESD electrodes made of stainless steel that contain mainly iron (70%) and other components including chromium (18%), nickel (10%), silicon (0.8%) and copper (0.3%). The metal particles with respect to carbon constitute an average volume ∼8%.

A typical electron diffraction image (Figure 3c) at the spot marked by the star (*) in Figure 3a demonstrates disordered nanographite. This was also confirmed by the Raman scattering spectrum (Figure 3d) with characteristic D and G peaks. A ratio of peak amplitudes provides an estimation of the scale of the sp3 phase particles among the disoriented carbon, which is ≤2 nm [18]. Obtaining the electronic diffraction pattern from the metallic nanosized particles was impossible due to their small size of 20 nm. The stability of the colloid as a whole allows us to assume that the metal particles are bound to carbon particles.

4. Seeding of Si substrates with the nanocarbon colloid

The colloid was used for seeding using the following methods: by treating the substrates in an ultrasonic (US) bath filled with the colloid and by evaporation a 5 mm colloidal layer above the substrate at room temperature. In the first case, under the influence of US vibrations, carbon nanoparticles can partially be combined into large agglutinates that violate the uniformity of the seeding layer. As a rule, aggregated particles fall out of the solution, but they can partially attach on the substrate. However, the second method is preferable because it does not form aggregates on the substrate. Both methods have common drawbacks due to drying of the moist substrate after drawing out from the colloid, which leads to local accumulations of carbon particles in the form of islands on the smooth silicon surface due to uneven evaporation of ethanol. In this case, the particles drift along the edges of colloidal stains during the drying process, as shown in the images (4a, b), which were taken in situ using a MMU-3 optical microscope. The dynamics of the colloid film upon drying is shown in the images due to the color interference fringes that reveal a profile of a thin inhomogeneous wet film on the µm scale. Large particles and bunched particles keep the ethanol in the immediate vicinity longer (Figure 4a). Thus, the circles (Figure 4a, c) or islands (Figure 4b, d) of the nanoparticles remain around them after the ethanol has dried.

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**Figure 3.** HRTEM image of a dried up colloid residue drop on a copper TEM grid (a) and its X-ray spectral elemental characteristics (b); electron diffraction pattern of the colloid residue (c) at spot * on image (a); and Raman spectrum of the colloid precipitate (d).
Figure 4. Optical micrographs: (a), (b) – interference fringes of white light in a thin film of ethanol on a Si substrate during drying of the colloid; (c), (d) – results of substrate seeding: (c) – a circle is shown around a big particle, (d) – clusters of particles are shown as islets

5. MPACVD diamond film deposition on silicon substrates and film characterization

The diamond film deposition was studied using a MPACVD reactor (ARDIS-100) [22] that is equipped with a magnetron generator of a continuous power of 2-6 kW at a frequency of 2.45 GHz. Experiments were conducted on the surface (100) of square polished silicon substrates (10 × 10 × 0.5 mm$^3$). The first pair was seeded under a 5 mm layer of a nanocarbon colloid, which was dried in air. The second pair of substrates was seeded using an ultrasonic apparatus in a nanodiamond powder suspension in isopropyl alcohol with a particle size of 50 µm at a concentration of 1 g/l. Figures 5 and 6 show the morphology of the grown diamond films and their Raman spectra, respectively. Diamond films were grown via different substrate seeding methods and using different modes of MPACVD deposition (see Table 1): microcrystalline diamond (MCD) mode (Figures 5a and 5c) and nanocrystalline diamond (NCD) mode (Figures 5b and 5d). This was done to compare the effect of the type of seeding on the quality of the films.

Table 1. Deposition conditions.

| Deposition mode | MW power, kW | P total, mm Hg | CH$_4$/H$_2$, % | Total gas flow, sccm | Substrate T, °C |
|----------------|--------------|----------------|----------------|---------------------|----------------|
| nanocrystal    | 3.0          | 90             | 4              | 500                 | 900–950        |
| microcrystal   | 4.5          | 60             | 4.5           | 524                 | 900–950        |

Figures 5a and 5b show that nanocarbon seeding in the form of islets reflects on the films grown as similar islands both via the MCD deposition mode and the NCD deposition mode, respectively. The morphologies of the island films (Figures 5a and 5b) and of the reference continuous films (Figures 5c and 5d) are similar under both deposition modes.

The Raman spectra were obtained using a LabRam Horiba spectrometer. The second harmonic of a YAG:Nd laser at a wavelength of 532 nm was used to excite the spectra. The scattered light was recorded in a backscattering geometry. The size of the laser focus was 2 µm, and spectra were recorded with a resolution of 2 cm$^{-1}$. Figure 6 shows the Raman spectra of films deposited for the MCD and NCD modes following the same order as they are presented in Figure 5. The Raman spectra in Figures 6a and 6c show considerable differences in the quality of the grown microcrystalline films (compare spectra 1 (Figure 6a) with 6 (Figure 6c). The reference samples that were seeded with a nanodiamond suspension (Figures 5c and 5d) show a high homogeneity in the films regardless of the deposition mode and despite a small disturbance (the chain of balls) due to a scratch on the substrate. A high narrow diamond peak at 1332 cm$^{-1}$ is observable in Figure 6c, whereas a less pronounced diamond peak with a D and G maxima and additional peaks at 1140 and 1470 cm$^{-1}$ are observable for the nanocarbon seeding (Figure 6a). The peaks are characteristic for trans-polyacetylene (TPA) [20].


At point 2, diamond is absent, and at point 3, between the islands, there is no carbon. A completely different result is observable in films for the NCD-deposition mode, where the spectra at points 4 and 5 for the island and 7 and 8 for continuous film are completely identical despite the differences in the types of seeding.

**Figure 5.** Morphology of the diamond films grown via seeding of two different types: (a, b) with the nanocarbon colloid and (c, d) with the nanodiamond powder colloid under different deposition modes: (a, c) – MCD mode, (b, d) – NCD mode.

Surprisingly, the Raman spectra for the NCD films with different colloidal seeding (Figures 6b and 6d) look identical to each other. These are also identical to the spectra for the NCD films \[21\] grown with a hot filament (HFCVD) on silicon with a previously deposited metal nanolayer: Cr, Mo, Nb, Ti, V and W.

Reproduction of the topology for a grown diamond film in the form of islands via islet seeding with a nanocarbon colloid showed that this result cannot be explained by the spontaneous nucleation of diamond on silicon; therefore, to obtain a continuous film of islands, it is necessary to increase the density of the condensed phase in the colloid and improve the wettability of the surface.

**Figure 6.** Raman spectra of the films. Films are arranged in the same order as in Figure 5. Raman spectra are indicated by numbers corresponding to points of Raman sounding (see Figure 5).

6. MPACVD growth of a solid free-standing microcrystalline diamond plate
A solid free-standing microcrystalline diamond plate was grown at CVD SPARK Ltd. on a silicon substrate (100) with a 57 mm diameter and a 490 µm thickness, despite the uneven seeding of the substrate with the nanocarbon colloid. The plate growth was carried out in the ARDIS-100 reactor at a
4.5 kW microwave power in a mixture of $\text{H}_2 / \text{CH}_4$ gases at a flow ratio 500 : 24 sccm (standard cubic centimeter per minute), respectively, and at a total pressure of 60 Torr. The substrate temperature was maintained at 830 °C. The growth time was 230 hours. The plate was separated from silicon substrate by etching in acids. The images in Figure 7 show the free-standing polycrystalline diamond plate.

Figure 7. Images of the free-standing polycrystalline diamond plate: general view (a) and front surface at different magnifications (b, c), view of silicon substrate surface after the carbon colloid seeding before the plate growth (d), reverse sides of the plate grown with the carbon colloid seeding (e) and the plate grown with the DND powder seeding (f).

On the left side, there are a general view of the plate and its front surface at different magnifications (b, c). On the right side, there is an image (d) of the silicon substrate surface on which the plate was grown just after seeding with the nanocarbon colloid. Figures 7e and 7f on the right show the reverse sides of the diamond plates: image (e) is the reverse side of the plate, which is the side of growth beginning from seeding, and image (f) shows the reverse side of another plate (given for comparison). This is also the side of growth after standard seeding with a nanodiamond powder colloid. The reverse sides (the interfaces) of both plates can be considered to be the surface of diamond film nucleation. Surface e was formed by large domains with a small number of pores. Interface f of the reference diamond plate has a more fractional and porous structure.

The polycrystalline diamond plate grown on the nanocarbon seeding has a solid free-standing microcrystalline diamond plate structure. Figure 8 shows the Raman spectra of the front and reverse sides of the diamond plate. Interestingly, the front surface of the diamond plate has a sufficient high quality, which is characterized by a narrow diamond peak at 1332 cm$^{-1}$; however, its opposite side (interface) is characterized as ordinary amorphous carbon by the D and G maxima.

Figure 8. Raman spectra of front (1) and reverse (2) sides of the diamond plate.
Thus, the solid free-standing plate grown on the seeding colloidal nanocarbon structure may have a microcrystalline diamond structure, despite the fact that its back side has an amorphous carbon structure.

7. Summary and outlook

It is impossible to exclude the possibility of the presence of diamond nucleation centers that are the form of nano-sized sp³ phases in the total mass of sp²-phased amorphous carbon, which serves as a seed for polycrystalline diamond growth of NCD-MCD structures depending on the growth regime. The possibility that metal nanoparticles or their carbides can also act as diamond nucleation centers cannot be excluded. The results in ref. [21] (in which nanodiamond film deposition on silicon substrates pre-seeded with metal nanoparticles (Cr and Ti) was studied) can serve as indirect confirmation of the active role of a metallic nanopowder or its carbides in a nanocarbon colloid for the nucleation of diamond.

Theoretical and experimental studies [22–24] have predicted the possibility of diamond nucleation under conditions that are considered to be metastable at moderate pressures and temperatures. The first attempt to understand the stability of diamonds on the nanoscale was reported by Badziag et al. [23], who computed the binding energy of diamond-like and graphite-like carbon clusters using fixed energy values for carbon–carbon and carbon–hydrogen bonds. They found that below a size of 3–6 nm diamond clusters are more stable than their graphitic counterparts. The relative stability of nanodiamond was checked depending on both the size and degree of coating of the nanodiamond surface with hydrogen until its complete absence. Calculations [22] showed that when the diamond size was below 3 nm, it was energetically more advantageous for it to have free surfaces without hydrogen compared with hydrogenated ones. This inability to retain hydrogen on the surface can be the reason for the limited growth of diamond up to larger grain sizes. Therefore, the curvature of nanodiamonds is the physical reason for their stability.

The further aim of our research is to detect nanodiamond crystallites in colloids used by HRTEM microscopy. We hope for a positive result, which will be based on experimental results [25] of the irradiation of ethanol with a femtosecond laser (1025 nm) at laser radiation energies above 300 µJ, which have shown that <5 nm nanodiamonds are formed directly in ethanol.

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