Emission properties of a nanodiamond composite

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Previous investigations have demonstrated promising field-emission properties of carbon layers composed of nano-size irregular low-aspect-ratio grains of sp^2 and/or sp^3 phases [1, 2]. To show high electron emission efficiency, these materials are subjected to preliminary field treatment at relatively low temperatures 200-400°C, which presumably leads to formation of emission sites through re-distribution of relatively "loose" atoms from boundaries, amorphous domains, defect clusters, etc. The main drawbacks of previously investigated materials of this type consisted in limited lifetime and emission instability.

In this work, we investigate a nanocomposite material that we expected to combine low-field emission with enhanced stability and longer performance time. The composite represents a nanodiamond powder with grains covered with CVD-deposited graphite nanolayer [3]. The graphite shells merge around the grain junctions, forming a solid well-conducting matrix and thus securing mechanical stability of the emitter in the field. The shells have definite structure of parallel graphene sheets, so that full number of defects and "loose" atoms is normally not very large. Yet, if the material is heated approximately to 800°C, re-crystallization of diamond starts, which can provide sufficient amount of mobile atoms to activate emission from the field-affected surface. Returning to room temperature, we can "freeze" the reconstructed state of active sites.

Emission parameters of the nanodiamond composite were found to be usual for materials of this class. Threshold current of 1 nA from a 0.05 cm^2 sample was typically obtained in 3-5 V/μm field. Current characteristics of emission deviated from Fowler-Nordheim model in the high-field area, which can be attributed to the presence of different types of emission centers. Complicated evolution of characteristics with temperature was observed and qualitatively explained.

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On the liquid carbon cluster structure

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There had been observed a formation of single carbine nanocrystals and whole eutectic colonies which took place at the liquid carbon non-equilibrium crystallization and was similar to the appearance of metastable phases at the solidification of the metal alloys [1]. These conditions were obtained at the crystallization of the unstable fragmentized liquid carbon film on the hard surface of the base HOPG face. h the aid of the laser pulse in a gas chamber at a pressure of the inert g. The melt was obtained by heating the face up to the melting temperature 4850Ê [2] wit as close to that one of the graphite triple point $P_{\text{òò}} \approx 10$ Ì Ï à.

The shrinkage porosity ca. 5%, found at the quasi-equilibrium liquid carbon solidification and its flowing beyond the limits of the laser beam spot evidence a significant increasing of the liquid carbon specific volume as compared with the graphite.

These results confirm the concept developed by the molecular dynamics approach and consisting in that the liquid carbon is an admixture of clusters with the structure similar to the carbine, diamond and graphite. The content of carbine-like clusters in this admixture can reach 60% at appropriate decreasing of the liquid carbon density [3].

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Adsorption of light hydrocarbons by single – wall carbon nanohorns

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Single –wall carbon nanohorns (SWNHs) were prepared by CO_2 laser ablation of carbon [1]. Aggregates of SWNHs can be prepared in macroscopic quantity and may be considered as material for storage of fuel such as methane and hydrogen [2, 3].

For the investigation of adsorption properties of SWNHs the gas chromatography method as well as the measurements of compound adsorption under static conditions were used. For chromatographic investigation SWNHs were deposited on inert support with small specific surface area.

Nitrogen adsorption as well as light hydrocarbons adsorption on SWNHs after oxidation on air are increased about two times in comparison with adsorption on initial sample owing to the opening of carbon nanotubes.

The comparison of retention volumes (constant of adsorption equilibrium at small coverage) of ethane, propane, n-butane and n-pentane on SWNHs with closed and opened nanotubes shows that they practically coincide in contrast of the differences in adsorption under static conditions. Probably it is connected with kinetic difficulties of penetration of molecules in nanopores of oxidized SWNHs during chromatographic process. This is supported by light hydrocarbon separations on initial and oxidized SWNHs.

The authors would like to express their appreciation to Dr. Sc. Masako Yudasaka for sample of SWNHs and also for valuable recommendations on their oxidation.

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Effects of modification of graphite by fullerenes, natural micron size diamonds and nanodiamonds at high-pressure high temperature synthesis of diamond

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We were studied the effects of fullerenes, detonation nanodiamonds and natural micron size diamonds to high-pressure high temperature metal catalyzed synthesis of industrial diamonds.

High-pressure of ~5 GPa was produced by a chamber consisting of two truncated hemispheres of ~2 cm^3 in volume. The synthesis time varied from 30 to 90 seconds and the temperature was up to 1650°C.

The output, strength and size distribution of diamonds were analyzed depending on synthesis conditions.

There are two ways of diamond growth when diamonds and nanodiamonds are added in the initial blend of graphite and metal. The first is spontaneous crystallization and following growth and the second is the building-up of added diamonds or nanodiamonds. In this case it is easy to see, that diamonds output increases but the diamonds strength is poor and the size distribution shows some features in some definite sizes.

It is more complicated when fullerenes are added. The diamonds output is also increase, but it is not build-up process. The output diamonds size distribution is practically the same and the strength of this diamonds is just a little smaller compared with that produced from initial blend.

Also, effects of starting pressure, relative pressure drop and linear displacement during the synthesis to the diamond output, strength and distribution are discussed.

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Nanocomposites based on diamonds and nanodiamonds with fullerenes

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We studied the sintering mechanisms and thermal conductivity of composites based on well purified detonation nanodiamonds. The thermal and electrical conductivities of composites from natural diamonds of 10-14 µm in size were also examined. Both types of composites were sintered at high pressures (5.0-7.0 GPa) and high temperatures (1200-2300°C) for 10-25 seconds. It was found that the thermal conductivity of composites from natural diamonds increased as the sintering temperature approached the diamond-graphite equilibrium in the pressure range of 4.5-6.5 GPa because of the surface graphitization of the diamond samples. Above the phase equilibrium temperature, the thermal conductivity was observed to decrease due to the sample bulk graphitization.

The maximum thermal conductivity for the nanodiamond samples was observed at approximately 1900°Ñ and 5.5 GPa. Higher temperatures caused sample damage at lowered pressures, which seems to be due to the nanodiamond transition to the nondiamond carbon phase possessing a lower density.

When we added 5 wt% of Ñ$_{60}$ fullerene to the initial nanodiamonds, the diamond transition to a nondiamond carbon-like state occurred at a temperature below 1400 °Ñ and the thermal conductivity increased from 50 to 100 W/(m*K).

Thermal conductivity was found to be about 50 W/(m*K) for the nanodiamonds samples and about 500 W/(m*K) for the microdiamonds.

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Derivatives $C_{21}H_{12}R_6$ of sumanene Ñ$_{21}$Í $_{12}$ as bowl-shaped precursors of derivatives R_6Ñ$_{60}$ fullerene Ñ$_{60}$ (R= ¾ ,H , Hal , CN)

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Modeling by the DFT of structure of five bowl-shaped molecules $C_{21}H_{12}R_6$ (R= H, Hal, CN), which are derivatives of sumanene Ñ$_{21}$Í $_{12}$ (Fig. 1a), and twenty times their complexes with moieties Cr(Ñ$_6$Í $_6$), $Cr(CO)_3$, Mo(Ñ$_6$Í $_6$) and $Mo(CO)_3$ was carried out. Groups R in molecules $C_{21}H_{12}R_6$ (R= H, Hal, CN) were added to carbon atoms of sumanene arranged to α-positions relative to central hexagon (Fig.1b). These molecules can be considered as precursors of derivatives R_6Ñ$_{60}$ ô óëëåðåí à Ñ$_{60}$. Stability of complexes Ì (Ñ$_6$Í $_6$)$C_{21}H_{12}R_6$ and Ì $(CO)_3C_{21}H_{12}R_6$ (M=Cr, Mo) was estimated. It was found that addition of moieties Ì (Ñ$_6$Í $_6$) è Ì $(CO)_3$ to molecule $C_{21}H_{12}$ with formation of η^6-π-bonds is greatly less profitably than in the case molecule $C_{21}H_{12}R_6$. Complexes the most preferably for synthesis were established. It was shown that Ì (Ñ$_6$Í $_6$)$C_{21}H_{12}R_6$ and Ì $(CO)_3C_{21}H_{12}R_6$ can be used for study of relative stability and electron structure of similar complexes of derivatives R_6Ñ$_{60}$ of Ñ$_{60}$ and also for investigation of influence curvature of conjugated system on physical-chemical properties of fullerene C_{60} derivatives.

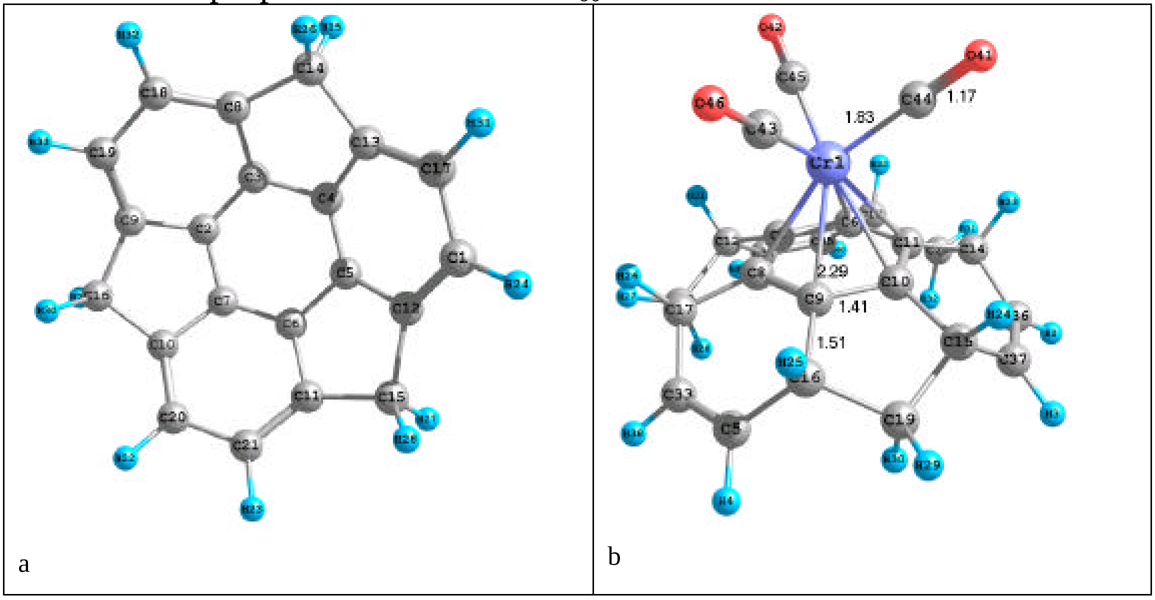

Figure 1. Sumanene $C_{21}H_{12}$ (a) and complex $Cr(CO)_3C_{21}H_{12}$ (b).

Structure of the most intensive Bragg’s reflex of carbon onions

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We studied structure of the most intensive Bragg’s reflex of carbon onions in the frames of classical kinematical theory of X-ray diffraction. Allowing for these results, a dramatic difference (factor 4-6) between size estimations for carbon onions by electron transmission microscopy and Scherrer method for X-ray diffraction reported in paper [1] may be explained.

Structure of Bragg’s reflex was analysed in the frames of classical kinematical theory of X-ray diffraction, where, the physical profile of a Bragg reflection is given by the convolution of the size and the lattice distortion profile. It is shown that lattice distortion profile for carbon onions structures appeared as non-Gaussian function demonstrating symmetry break. This asymmetry was suggested to appear in the course of nanodiamond – carbon onions phase transition.

Our analysis allowed determining size distribution function and its moments for carbon onions. Average sizes for carbon onions was shown to vary from 100 A and 130 A for surface-weighted and volume-weighted means, correspondingly. Those values are in a good agreement with high-resolution electron microscopy technique.

This approach allows us also to extract trend appearing for diffraction angles $2\theta<20^o$. We demonstrated that the extracted trend might be fitted by Voight profile with typical width of its size-dependent part; corresponding to onions sizes, which coincide exactly to those, appeared in previous analysis.

Independently important result consists in attributing observed linear parts of log-log plot of this trend to the property of the Voight function than to fractal structure of the investigating material.

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Size-distribution function of ultradisperse diamonds

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The aim of this work is to develop an approach to extraction of the size-distribution function of ultradisperse diamonds from their X-ray diffraction profiles. Literature data for X-ray diffraction profile of ultradisperse diamonds are surveying. The structure of Bragg's reflex are analyzing in the frames of classical kinematical theory of X-ray diffraction, where, the physical profile of a Bragg reflection is given by the convolution of the size and the lattice distortion profile. We have fulfilled deconvolution of X-ray diffraction profiles on Gaussian and Lorentzian components using best-fit technique of Voight function to the experimental diffraction profile. Lorentzian component was used to derive size distribution function (1) and its moments ((2) and (3)) for ultradisperse nanodiamonds, results are depicted in Fig.1. It is seen that average sizes for carbon nanotubes vary from 40 A and 60 A for surface-weighted (2) and volume-weighted (3) means. Derived distribution functions are noticeable different from reported earlier [1].

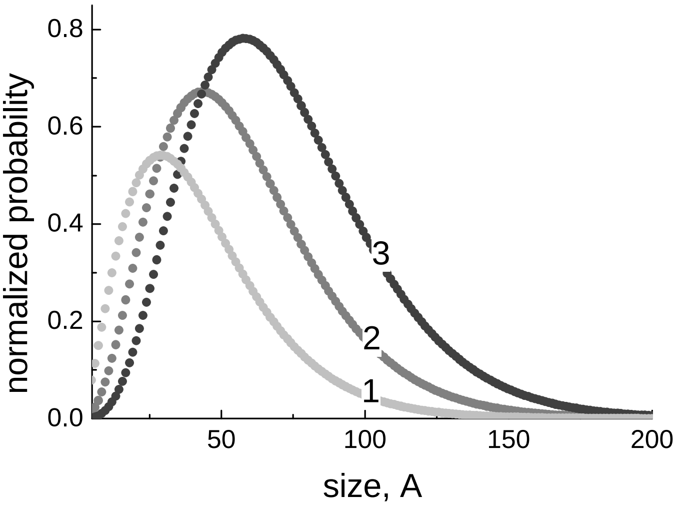

Figure 1. Size-distribution function of ultradisperse nanodiamond crystals (1) and its surface- (2) and area- weighted (3) means distributions.

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