INVESTIGATION OF OPTICAL AND STRUCTURAL CHARACTERISTICS OF THE VARIOUS MEDIAN SIZES LUMINESCENT DIAMONDS PRODUCED BY THE SHOCK WAVE SYNTHESIS WITH FOLLOWING GRINDING

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Abstract

The intense 738 nm narrow band luminescence of the SiV-centers for polycrystalline nanodiamonds produced by shock wave synthesis followed by grinding and separation into fractions with median sizes from 25 to 1000 nm are observed for all fractions. Polycrystals composed of tightly connected differently oriented diamond nanocrystals with mean sizes of 10-15 nm were formed by merging the boundary areas of the crystal lattices of adjacent nanocrystals. Size-dependent structural and luminescent properties were studied by comparative Raman and luminescence spectroscopy. Analysis of the Raman spectra from luminescent diamonds with median sizes from 1000 nm to 180 nm shows damage of the intergranular layers with the increase of amorphous carbon content. Raman spectroscopy for the fractions from 180 nm to 25 nm shows damage of the cubic diamond nanocrystals with the appearance of disordered carbon structures, which increases with decreasing median size accompanied with a strong decrease of the luminescent intensity. It was found than SiV luminescence intensity has a maximum at the median size of about 180 nm that is controlled by competition between deactivation of the SiV-centers by defects in the diamond nanocrystal lattice and nonradiative recombination centers in the volume of the intergranular layers.

Keywords: Nanodiamonds, SiV-center

1. INTRODACTION

Diamonds can be synthesised by different methods including CVD techniques and static synthesis at high pressure (up to 7 GPa) and high temperature (up to 2200°C) which have found broad applications in the industry. This work presents diamonds synthesised by shock wave synthesis. Diamond powders were manufactured by Microdiamant USA, and commercially distributed by L. M. Van Moppes & Sons SA (Geneva, Switzerland) under the trade name Super Syndia^{TM} SSX,[1]. According to the manufacturer a powder of polycrystalline diamond particles of micron size (10-60 µm) consisting of individual diamond nanocrystals with sizes not exceeding 20-25 nm each. Diamond nanocrystals are tightly bound together by means of the spliced edges of the crystal lattices and by covalent bonds of shorter atomic groups existing on the grain boundaries. Diamond powders was grinded with following separation to powders of polycrystals with smaller different median sizes (25-1000 nm). Rapid synthesis and direct conversion of graphite to diamond in air results in the formation of fairly large numbers of defects in the presence of impurity atoms in the crystalline lattice of polycrystalline. This can leads to the appearance of NV- and SiV-centers, for example, which can be identified by electron paramagnetic resonance [2] and luminescence spectroscopy. Probably Content of luminescent NV- or SiV-centers can be controlled by with synthesis shock wave parameters. To investigate dependencies and make structural characterization Raman and luminescence spectroscopy are particularly adequate as they permit the quick and contactless investigation of the samples without disturbing the structure of the constituent materials.

2. EXPERIMENTAL

We have investigated set of polycrystalline diamond produced by shock wave synthesis powders with a median size of diamond polycrystals from 1000 to 25 nanometers was obtained by step-by-step fractionation of once milled starting powder. Size fractionation of the submicron dust was accomplished by centrifugation or sedimentation in water the micron fraction with median particle size 1-2 microns. According elemental analysis there are traces of graphite phase and content of other elements as follows: Fe - 9000 ppm, Si - 4870 ppm, Ca - 790 ppm, Al - 260 ppm, Cu - 170 ppm, Mg - 150 ppm, Ni - 50 ppm, Ti - 30 ppm, Mn - 30 ppm. Each fraction was subsequently extra-purified and then washed in rinsing water several times. According the XRF data, in the extra-purified nanodiamonds there are some content of silicon about 5-6 ppm level, while the content of other metal pollutants (except alkaline metals) is below 1-3 ppm. More detailed description of samples described if ref. [3]

For a clear understanding of structure on **Figure 1** shown characteristic HRTEM images of the polycrystalline diamond fraction. Diamond nanocrystal domain was analyzed by using the method similar to ref. 4, which uses the FFT spots to determine the domains. Cubic diamond crystallites and twinning boundaries are clearly seen on the images.

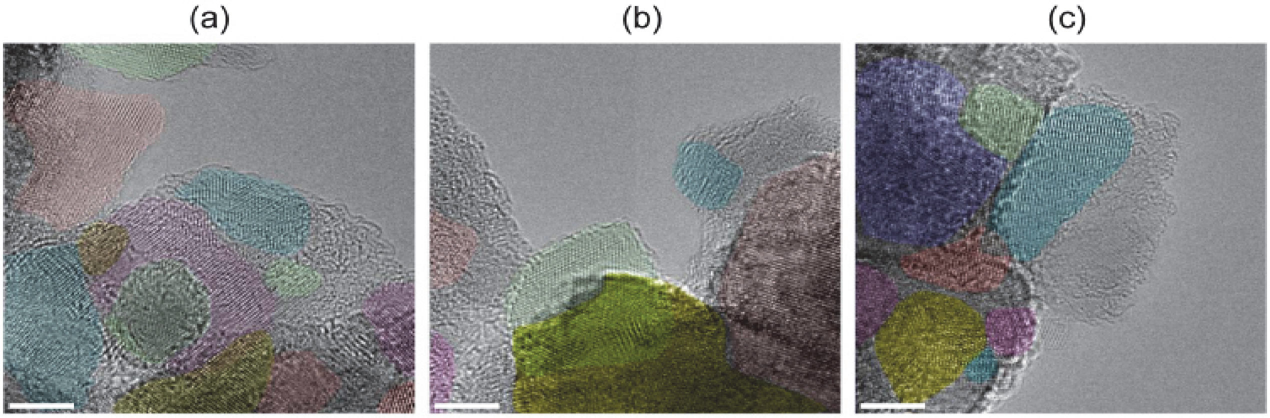

Figure 1 (a) - (c) Characteristic HRTEM images of the smalest grade of polycrystalline diamond fraction. Areas shaded in different colors correspond to the individual crystallites with different orientation. Scale bars of 4 nm are shown

The secondary emission spectrum 500-800 nm spectral range from diamond powder with median size ~180 nm is shown on **Figure 3. Figure 3** also shows also an example of the deconvolution of the luminescence background. Luminescence broadband background observed in secondary emission spectra also usual for diamonds particles produced both by detonation techniques [5] and CVD methods [6] and is attributed to a broad orange-to-red PL caused by NV. This deconvolution was performed for the spectra of all samples for subtracting the luminescence background. The spectrum shows characteristic photoluminescence (PL) and Raman bands observed in the spectra of all fractions of polycrystalline diamonds. The 738 nm narrow line observed in the spectra of all fractions is attributed to PL from Si-V colour centers formed by the intercalation of silicon atoms into the crystal lattice of diamond particles.

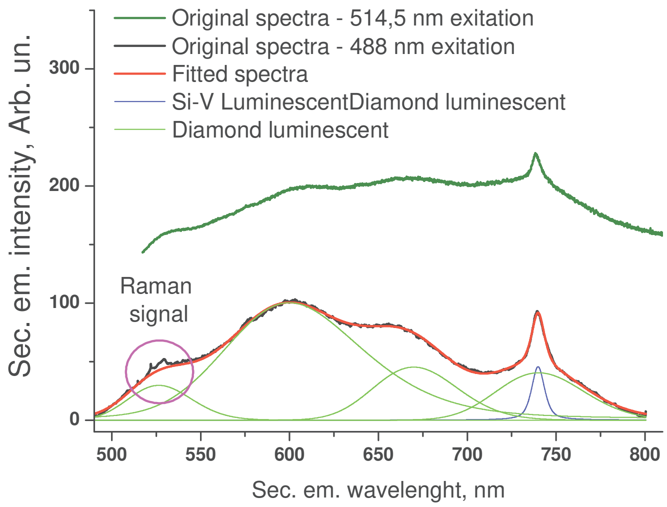

Figure 2 Characteristic spectrum of secondary emission polycrystalline diamond fraction for excitation wavelength of 488 and 514 nm. The deconvolution of the broad PL background is shown for spectrum with wavelength of 488. The pink circle shows the region of the Raman spectrum

Figure 3 presented Si-V center PL (a) and Raman signal (b) for few median sizes of nanodiamond powder after subtraction of broad background luminescence. **Figure 3a** displays a characteristic set of Raman spectra from samples of diamond polycrystals with different median size. Bands assignment for Raman spectra shown well-known Raman bands such as diamond Raman band [6] at about 1332 cm^{-1} and bands of disordered nanocarbon structures [7]. These characteristic bands were dominate for all spectra. It is worth noting that Raman cross-section for diamond at 488 nm excitation wavelength is smaller by more than one order of magnitude than for sp_2 carbon. nanostructures we can conclude that the structure of the studied samples is dominated by the diamond phase. Bands of disordered nanocarbons place at ~1350 cm^{-1} (D), ~1530 cm^{-1} (A), ~1587 cm^{-1} (G), and ~1625 cm^{-1} (D'). The presence of the G-band in the spectra points out to the presence of sp2-bonded C atoms. The D and D' bands correspond to the breathing vibration of aromatic rings in the carbon network and their intensities are proportional to the degree of structural disorder in graphite-like structures[7].

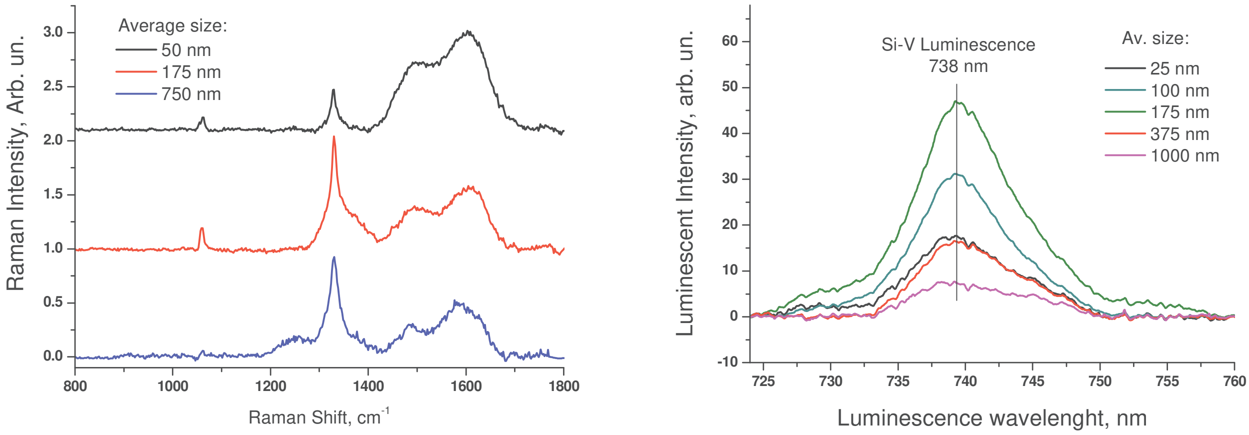

Figure 3 (a) Representative set of Raman spectra of the polycrystalline diamond fractions with different median size for excitation wavelength 488 nm. (b) Representative set of Si-V center PL spectra of the polycrystalline diamond fractions with different median size for excitation wavelength 488 nm

Figure 3b presents spectrum of PL after subtraction of broad background luminescence. It is clearly seen that PL intensity depends of median size of nanodiamods. To better understanding graph was constructed between the mean size and intensity of Si-V center PL which is presented on **Figure 4.**

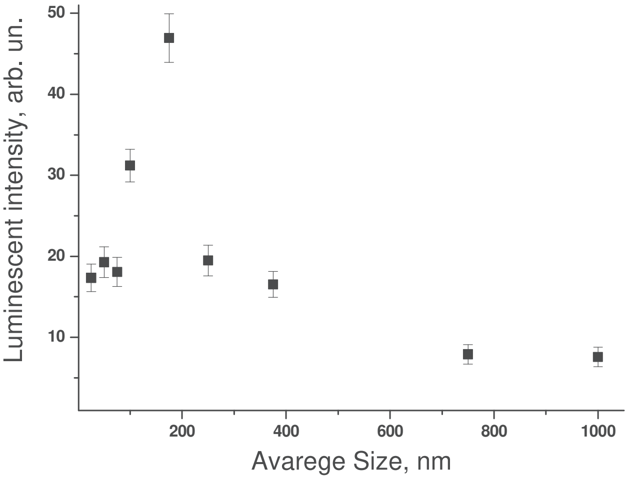

Figure 4 Size dependence of the integral intensity of the Si-V center luminescence band. Excitation laser wavelength: 488 nm

3. DISCUSSION

The size dependences of the SiV-center luminescence band at 738 nm shown in **Figure 4** presence of a clear maximum at ZM = 180 nm. The maximum can be caused by competition between two processes taking place in the samples during grinding. The presence of two different phases of diamond, where each can be responsible for a process can give rise to a maximum. There are two diamond phases in all samples with different median size: cubic diamond in the nanocrystals and hexagonal diamond, located in the intergranular layers. The diamond Raman band intensity reflects the content of diamond crystal phases. It is cleary seen that till the maximum point of PL for the samples with median sized ~180 nm there is no sufficient changes in structure of raman diamond band at 1332 cm^{-1}. For the samples with median sizes less than 180nm we can see decreasing of raman signal intense. This process can be attributed to increasing amount of defects in cubic diamond phase. In support of this assumption we can see increasing of signal from disordered nanocarbons which is appears from damaged cubic diamond phase. For the bigger size we don't see sufficient changes in strusture on raman spectra. We can make a assumption that decresing of size for the samples till 180nm providing by destroing twining boundaries between diamond nanocrystals. The latter was associated to the formation of recombination centers inside covalent bonds of shorter atomic groups existing on the grain boundaries, opening non-radiative decay channels in disordered regions. At the same time, the decrease of the PL intensity upon increase of size from 180 nm to 1000 nm requires additional assumptions.

4. CONCLUSION

In this work Raman and luminescence spectroscopy were used for investigating polycrystalline diamond powders produced by shock wave synthesis followed by grinding and separation into fractions of different polycrystal median size in the range 25-1000 nm. The TEM data used to estimate the diamond polycrystals structure which consist of 10-15 nm nanocrystals with thin (2-3 nm) intergranular layers. A distinctive feature of the diamond powders studied is the presence of a narrow intense PL band of SiV centers at 738 nm. It is the first case of Si-V color centers found in diamonds produced by short duration dynamic synthesis. Was cleary shown that Si-V center PL intensity depends on the polycrystalline powder mean size and has a maximum at size ≈180 nm. This maximum is the result of competition between two nonradiative channels luminescence quenching the opposite depending on the average size of a polycrystalline powder. The process of increasing the luminescence with size reduction from 1000 nm to 180 nm is associated with a nonradiative recombinatio centers n in the volume of the intergranular layers. The concentration of these recombination centers decreases with decrease in the average size of the polycrystal which causes PL increase up to an median size of 180 nm. Further grinding resulting damage of crystal structure of the nanocrystals and the formation of additional defects with increasing amount of disordered carbon. The concentration of defects in crystal structure increases with decreasing size of the polycrystal and leads to suppression of luminescence.

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