DIAMOND NANOCRYSTALS MADE FROM FULLERENE SOOT

M.V.Baidakova, V.Yu.Davidov, S.V.Kidalov, A.V.Yashin, A.Ya.Vul'
Ioffe Physico-Technical Institute, 26 Polytechnicheskaya st.,
St.Petersburg 194021, Russia

Introduction

An attractive application of fullerenes is use them as a raw material for making diamond and some novel superhard substances even superior to diamonds [1,2]. This possibility was confirmed experimentally; and in many of these studies, C_{60}, or the C_{60} - C_{70} mixture were subjected to compression (up to 20 GPa) by a shock load [1,3,4]. The characteristic size of diamond crystallites was reported in [3] to be tens of nanometers.

Here we present the results of diamond synthesis from fullerene - containing soot (FCS) and fullerene extract using a standard technology for diamond synthesis from graphite.

Experimental details

FCS and extract (C60/C70 = 85/15) were obtained by usual Huffman-Krätschmer method. The soluble fraction was extracted with toluene or xylene. The composition of the FCS and fullerene extract was determined by mass-spectroscopy. After press-baking for several minutes, the diamond-containing cake was treated chemically to isolated diamonds. The diamond crystals obtained were separated by grain size, each fraction was weighed and tested for compression resistance.

Three sets of experiments were carried out: when the FCS was mixed to with some amount of graphite, when the FCS was used as an alone source of carbon and when a source of carbon was fullerene extract.

When FCS was used as an alone source of carbon diamonds did not form. When a source of carbon was fullerene extract diamonds with the size about 5-10 μm were forming. Diamonds have been formed when the graphite was added to the FCS.

The samples N977 (100) and N977(200) with size 100 μm and 200 μm were obtained from a mixture of FCS and graphite.

The samples N983 (100), N983(160) and N983(260) with size 100, 160 and 200 μm were obtained from thouse mixture when the the higher content of fullerenes.

Results and Discussion

Raman spectroscopy is the most widely used technique for characteristing diamond materials. This technique yields information about the relation sp^3 (diamond) to sp^2 (graphite) bonding and is sensitive to the presence of defects in the crystal lattice.

Micro-Raman measurements were carried out at room temperature using the double grating monochromator DFS-24 equiped with computer conrolled data acqusition. The Raman spectra were excited by an argon laser (L=488 nm); the power at the sample was 5mW in a spot ~ 20 μm in diameter A natural IIa single-crystal diamond was used as a reference.
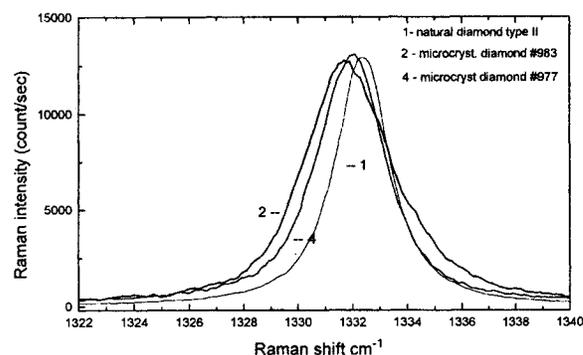
Figure 1. Raman spectra of natural diamond (type II and the diamond nanocrystals made from fullerene soot.

Figure.1 display the Raman spectra obtained from the synthetic microcrystalline diamond. The existence of sharp feature near 1332 cm^{-1} demonstrates the presence of diamond in powder. The triply degenerate phonon of F_{2g} symmetry is normally observed at 1332.5 cm^{-1} in high-quality single-crystal diamond. The other features in the spectrum that are characteristic for nondiamond forms of carbon (1580 cm^{-1} for graphite and 1360 cm^{-1} for glassy carbon) are not observed. Moreover it is known, that the Raman scattering efficiency for the sp^2-bonded graphite is more than 50 times greater than for the sp^3-bonded diamond. Taking this fact into account, we can conclude that the diamond

powder under study is pure diamond without any traces of graphite.

The feature that is most relevant to the presence of defects in diamond crystal lattice is full-width at half-maximum (FWHM) of the first-order phonon line in diamond. The profile of the phonon line of high-quality single-crystal diamond is well described by a Lorentzian with FWHM of 1.8 cm^{-1}. An increase in defect density shifts the 1332.5 cm^{-1} line frequency and increases the FWHM.

The Raman spectra to be shown on Figure1 were carried out under the same conditions for both samples. The instrumental profile of the spectrometer can make an important contribution into measured line shape. In our case the instrumental profile was fitted by a Gaussian function with FWHM of 0.25 cm^{-1} and its contribution into measured phonon line was small. The experimental Raman spectrum of the natural diamond shown on Figure 1 can be fitted rather well with a Lorentzian function with FWHM of 2.01 cm^{-1} and maximum at frequency 1332.4 cm^{-1}. As can be seen the phonon line of sample N977 remains simmetric and its line shape as well fitted by Lorentzian with FWHM of 2.84 cm^{-1}. Simultaneously a small low-fequency shift of phonon line of 0.5 cm^{-1} is observed. the Raman spectrum of the sample N983 can also be fitted by Lorenzian with FWHM of 3.51 cm^{-1} and maximum at frequency 1331.5 cm^{-1}. It should be noted that the Lorenzian approximation in this case is not so good as for the sample N977 and low-frequency shift of phonon line of 0.9cm^{-1} is observed.

The changes of FWHM of phonon line and its position in Raman spectrum provide evidence for the existence of defects in the synthetic diamond crystal lattice. The contributions to the phonon line shape caused by defects can be manifested in the various forms. A Lorenzian line shape with broadening caused by a decrease in phonon lifetime can appear, or an asymmetric line shape appeares due to the relaxation of the k=0 wave-vector selection rule. A Gaussian profile may be produced due to the lattice stress caused by defects . These contributions grow with an increase in defect density. Our data however show that phonon line of microcrystal sample N977 consistently displays symmetric Lorenzian profile with only a small increase of FWHM of 0.8cm^{-1} and a small low-frequency shift. We can therefore conclude, that the synthesized diamond has only internal stress and low defect density.

X-ray diffraction (XRD) pattern for the samples (N977, N983) contains three main difraction peaks These peaks correspond to three phases of diamond with a slight different lattice constants: a_0= 3.565A, a_1 =3.560A , a_2=3.572A. a_0 is nearly equal to lattice constant of natural diamond a=3.5667A. That is why changes in lattice constants we relate to internal stress in diamond microcrystals. It was shown that an increase of fullerene content reduces a deviation of lattice constants producing diamonds from the lattice constant of natural diamond with the growing of the size of diamond microcrystal.

Interesting to compare these data to results, received as metal desolving carbon and initial raw material to put in layers [5] . In this case experiments showed that the graphite-like soot phase and graphite transforms to diamond above 2 GPa more intensively than from graphite .The diamond crystal size at optimal conditions varied between 100 and 800 micrometer, the yield of large crystals (600-800 µm) being 33 wight percent. The Raman scattering line at the frequency 1332 cm^{-1} of 2 cm^{-1} wide indicates on the presence of a diamond high quality diamond structure. The unexpected result of ourexperiments was that diamond crystals were obtained without any catalyst from fullerene extract in contrast to the result [6].

Conclusion

In summar, we have found that using of fullerene - containing soot as initial raw material at synthesis of diamonds is interesting for practical applications.

References

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