

# XRD Analysis of Synthetic Diamond Powders Irradiated with Electrons

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Powders of synthetic diamond with low strength were sorted on sets with a different grain size. The synthetic diamond sets had various crushing strengths and morphology. They were irradiated with high energy electrons (6.5 MeV,  $D = 2 \times 10^{19} \text{ cm}^{-2}$ ) and analyzed using X-ray diffraction (Cu  $K_\alpha$ ) before and after irradiation. As established from nonlinearity of the  $a(\theta) = f\{R(\theta)\}$  dependences and observed extra splittings in X-ray diffraction patterns (in addition to  $\alpha_1$ - $\alpha_2$  doublets), crystal lattice of synthetic diamond from different sets was variously distorted. Irradiation led to decreasing distortions more significantly, the higher the initial strength of the set was. The made conclusions coincide well with our previous results on synthetic diamond powders which were irradiated under various softer conditions with direct measurements of synthetic diamond crushing strength without X-ray diffraction analysis. X-ray diffraction allows to presort synthetic diamond of critically low relative mechanical strength as well as evaluate resistance of diamond crystal lattice against heavy irradiation and other external impacts.

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## 1. Introduction

Diamond as superhard material is widely used in industrial applications. As a wide bandgap semiconductor ( $E_g = 5.5 \text{ eV}$ ) diamond in natural (ND) and synthetic (SD) forms is used in electronic devices. Only synthetic cubic boron nitride (cBN) ( $E_g = 6.4 \text{ eV}$ ) as the closest analogue of diamond, is superior to diamond in thermal, radiative and chemical stability. Both materials can be synthesized under high pressure–high temperature (HPHT) conditions.

Radiation resistance of electronic devices is guaranteed by stability of their functional materials when they have to withstand the harsh radiation environment. In the case of diamond, degradation of the mechanical strength is the direct and critical criterion for link establishment with its radiation resistance.

The present work is aimed to development of the evaluation method of the SD relative mechanical strength and the material's radiation resistance.

Due to defects and impurities, such properties of SD and cBN as thermal conductivity, mechanical strength and radiative resistance are worse than expected. Defects in diamond have been investigated with various spectroscopies (photoluminescence (PL), cathodoluminescence (CL), ESR, Raman, IR). A lot of optically active and paramagnetic defects in ND and SD were discovered and confirmed [1, 2]. It is established that nitrogen differently influences the materials functional properties in dependence on the form and concentration of nitrogen inclusions in diamond. Additional imperfections are ex-

pected due to large sizes of catalyst atoms and doping impurities incorporated into SD crystal lattice. As shown in [3], ferromagnetic impurities are non-uniformly introduced into SD (formed as powders of low strength) and in larger concentration than nitrogen, that cause variations of the materials mechanical strength.

The question arises about presorting SD of average quality in a simplest way, if the material has impurities or should be subjected to external impacts. X-ray diffraction (XRD) analysis allows to characterize crystal lattice structure of SD and cBN. As it was recently discovered, the crystal lattice of cBN can be differently distorted by the rare earth ions ( $\text{RE}^{3+}$ ) [4–6]. Even intrinsic boron leads to crystalline distortion in cBN [7].

We distinguish here the effects of strains in diamond crystal lattice from its crystal distortions. For uniform strains, sharp peaks of the sample's XRD pattern naturally shift in position, the stronger the larger the Bragg angle increases. For non-uniform strains, peaks broaden. In both cases peak shape remain symmetric. Please pay attention to symmetric (440) peaks from different faces with various nitrogen concentration ( $N = 10^6 \text{ cm}^{-3} - (88 \pm 7) \times 10^6 \text{ cm}^{-3}$ ), which were observed in the XRD patterns of very pure SD single crystals [8]. On the other hand, distortions of cubic crystal lattice lead to lowering its cubic symmetry. In this case, in the XRD pattern extra splittings of basic peaks of cubic structure appear [9]. The splittings follow the appearance of new ( $hkl$ ) planes  $d$ -spacing caused by breaking rule for the multiplicity factor  $m$ . The peaks of XRD pattern from a perfect crystal lattice do not split under monochromatic Roentgen irradiation. Referring to [8], we cannot expect there any distortion of SD crystal lattice.

In the previous work [10], we obtained strengthening in SD industrial powders after irradiation with 4 MeV elec-

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trons with fluencies ranging from  $D = 10^{17}$  to  $2 \times 10^{18} \text{ cm}^{-2}$  in vacuum and  $\text{CO}_2$  atmosphere. In this work, we increase energy and fluence of irradiating electrons to establish the fluence for breaking SD strength without the latter's direct measurements. We try to develop interdependence between relative strength of synthesized SD powders and peak shape in their XRD patterns.

## 2. Experimental details and results

Low strength SD industrial powders were synthesized under the HPHT conditions using a NiMn catalyst. Powders were sorted onto sets with the grain sizes 80/63, 100/80, 125/100, 160/125, 200/160  $\mu\text{m}$  using the sieves analysis. The concentrations of dispersive nitrogen in SD in the range  $(1.8\text{--}2.4) \times 10^{18} \text{ cm}^{-3}$  were evaluated from ESR. The electron irradiation of the SD sets was performed under vacuum condition using 6.5 MeV electrons ( $D = 2 \times 10^{19} \text{ cm}^{-2}$ ) at  $T = 450 \text{ K}$ . Morphological features of SD grains in the sets (Fig. 1) were visualized by scanning electron microscopy (SEM). Crushing strength of each SD set was measured using a standard grain crushing method (Fig. 2). Two industrial SD sets were investigated which showed very close results. As can be seen from Figs. 1 and 2, the worse the morphology of SD grains, the lower is the strength of grains, and the 100/80 set possesses the maximal crushing strength. Generally, the most perfect morphology and strength are characteristic of crystallization centers of SD which appear in the most equilibrium thermodynamic conditions.

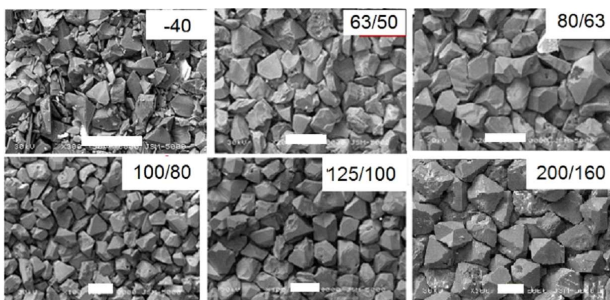


Fig. 1. SEM images of SD sets. Length of a white bar is equal to 100  $\mu\text{m}$ .

XRD patterns from the SD sets before and after irradiation were taken repeatedly with a step of  $0.01^\circ/\text{min}$  using a D8 Advance Bruker AXS instrument with Cu K radiation. For measurements, equal masses of powders were placed into standard cuvettes. *The rotation option* of samples was used to avoid random errors and to consider contribution of all crystallographic planes of  $\{hkl\}$  multiplicity into each  $(hkl)$  reflex of XRD patterns.

The XRD patterns from the SD sets were represented by (111), (220), (311), (331) basic peaks of various relative intensities, which were related to a diamond crystal lattice. It was assumed that SD could be textured or its crystal lattice was distorted [5].

It is known that for a perfect crystal lattice, the dependence  $a(\theta) = f\{R(\theta)\}$  is linear, where  $a(\theta)$  is the

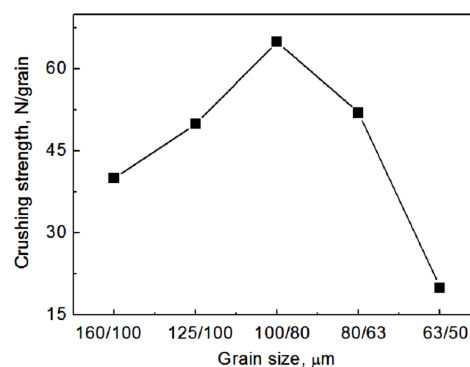


Fig. 2. Mechanical (crushing) strength of SD sets (N/grain) in dependence on size of SD grains in the set.

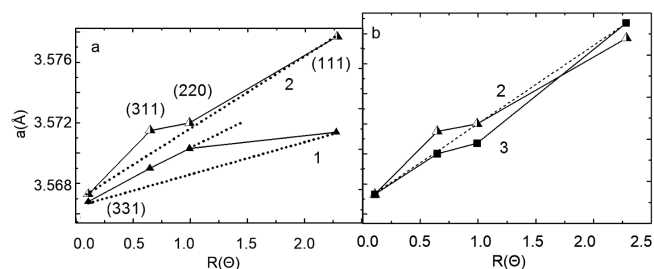


Fig. 3. Dependences of SD lattice constant on the Raily function for 100/80 SD set before (1) and after irradiation (2) (a), of 100/80 (2) and 200/160 (3) SD sets after irradiation (b). All under the rotation option.

lattice constant and  $R(\theta)$  is the Raily function, both calculated for each peak of a XRD pattern from the crystal lattice. If not, the crystal lattice is distorted [5, 7]. As established, the dependences  $a(\theta) = f\{R(\theta)\}$  are variously nonlinear for different SD sets (*the rotation option* was applied in all cases). This distinguishes our case from uniform strains of SD crystal lattice in [8]. The dependence for the 100/80 set before and after irradiation is presented in Fig. 3a and in Fig. 3b as compared to the 200/10 set.

Irradiation of SD sets led to changes of nonlinear character of dependences  $a(\theta) = f\{R(\theta)\}$ . They turned to linear character (more or less for different SD sets) and mostly due to the increase of interplanar  $d_{111}$ -spacings (Fig. 3b). The crystal lattice of SD after irradiation became more perfect because its distortions decreased due to impurities redistribution among thermodynamically more favorable positions. More evidently, the 100/80 set has the enhanced perfection of SD crystal lattice.

The obtained results were confirmed by discovering extra splittings of basic peaks in the sets' XRD pattern, which are complementary to the  $\alpha_1\text{--}\alpha_2$  doublets for Cu  $K_\alpha$  irradiation. First, some extra splittings of basic peaks could be visibly discovered (Fig. 4a, the inset). Secondly, the results were refined under *the rotation option* (Fig. 4a,b), and asymmetric basic peaks were decomposed onto Gaussians using computer program to

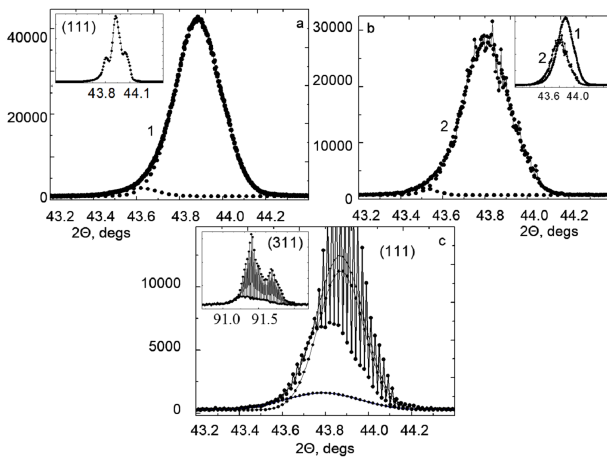


Fig. 4. The (111) peaks in XRD patterns from the 100/80 SD set before (a) and after (b) irradiation, in the insets without the rotation option (a), before (1) and after irradiation (2) under the rotation option (b); from the 200/160 set after irradiation (c), in the inset peak (331), under rotation option. Results of Gaussian deconvolution are shown as dotted lines.

visualize the splittings. Generally, the extra splittings varied from one set to another, as well as before and after irradiation. Such splittings are not characteristic for a perfect cubic crystal lattice. They are the proof that the lattice is distorted. The larger number of extra splittings, the higher is symmetry of distortions (tetragonal, trigonal, etc.).

As follows from Fig. 4, the asymmetrical peak (111) in the XRD pattern from the 100/80 SD set, is split onto basic and additional peaks (non-resolved  $\alpha_1$ - $\alpha_2$  doublets). The broad and more intense additional peak proves that more the  $d_{111}$ -spacings in non-irradiated SD crystal lattice are changed non-uniformly. After the irradiation, the additional peak of smaller intensity and width, and peak angle position, demonstrate that a number of equal interplanar  $d_{111}$ -spacings increased and the factual random distortion decreased, but the actual mathematical value of distortion is increased (for example:  $\Delta\gamma$  for trigonal distortion,  $\gamma = 90^\circ$  for cubic crystal lattice). We have supposed here that a type of distortion after SD irradiation is not changed. As a general conclusion, SD inside the 100/80 set enhances its perfection.

Concerning the 200/160 set, it contained very large grains which grow very quickly and have the lowest initial strength. After irradiation, the total intensity of XRD pattern is still extremely low. The additional peaks from the (111) and (311) splittings (Fig. 4c and the inset) illustrate the existence of the factual random distortions which continue to cover a lot of  $d_{111}$  and  $d_{311}$  spacings. In this case even after irradiation of the 200/160 set, the SD crystal lattice is more strained and distorted as compared to that in the 100/80 set. The dependences  $a(\theta) = f\{R(\theta)\}$  (Fig. 3b) testify that an average lattice parameter of SD crystal lattice in the irradiated 100/80 set increased more than in the 200/160 set.

### 3. Conclusions

Industrial powders of synthetic diamond of low strength were sorted into sets of different grain sizes with various crushing strength and morphology. The SD sets were investigated by XRD using the rotation option of samples. Nonlinear dependences  $a(\theta) = f\{R(\theta)\}$ , where  $a(\theta)$  is the lattice constant and  $R(\theta)$  is the Raley function, and the discovered extra splittings (additional to the  $\alpha_1$ - $\alpha_2$  doublets on Cu  $K_\alpha$ ) in the XRD patterns from the SD sets, testified that crystal lattice of diamond in sets was variously distorted. It looks like that the materials represent differently disordered solid solutions of impurities in diamond. The higher degree of disordering of SD crystal lattice, the lower the strength of the corresponding SD set. As compared to our previous experiments, irradiation of the SD sets with electrons of higher energy and at larger fluence ( $E = 6.5$  MeV,  $D = 2 \times 10^{19}$  cm $^{-2}$ ) still leads to strengthening SD crystal lattice, the more effective, the higher initial strength of the SD set.

Thus, the XRD analysis allows to presort synthetic diamond material with critically low relative mechanical strength as well as to evaluate resistance of diamond against irradiation and other external impacts.

### References

- [1] A.M. Zaitsev, *Optical Properties of Diamond: A Data Handbook*, Springer, Berlin 2010, p. 502.
- [2] *Properties and Growth of Diamond*, Ed. G. Davies, Run Press Ltd., Exeter 1994, p. 437.
- [3] G.P. Bogatirova, V.B. Maevski, G.D. Ilmitskaja, G.F. Nevstruev, V.N. Tkach, I.N. Zaitseva, *Superhard Materials (Ukraine)* **28** (4), 56 (2006).
- [4] E.M. Shishonok, *Cubic Boron Nitride: Raman and Luminescence Investigations, Prospects for Use in Opto- and Microelectronics*, Publ. Center of BSU, Minsk 2009, p. 267 (in English).
- [5] E.M. Shishonok, J.W. Steeds, A.V. Pysk, E.O. Mosenov, O.R. Abdullaev, A.S. Yakunin, D.M. Zhigunov, *Powder Metall. Met. Ceram.* **50**, 754 (2012).
- [6] E.M. Shishonok, V.G. Luhn, *Proc. BSTU Phys.-Math. Sci. Inform.* **6**, 62 (2013) (in Russian).
- [7] S.P. Bogdanov, *Proc. All-Russian Scientific-Technical Conf. "Electrothermia 2008"*, 2008, p. 92 (in Russian).
- [8] A.R. Lang, M. Moore, A.P.W. Makepeace, W. Wierchowski, C.M. Welbourn, *Philos. Trans. R. Soc. Lond. A* **337**, 497 (1991).
- [9] A.M. Abakumov, *Lectura X-2006CD*.
- [10] V.B. Shipilo, E.M. Shishonok, F.P. Korshunov, G.P. Popelnuk, Patent of Republic of Belarus No 2282, *Official Bulletin of National Center of Intellectual Property*, Vol. 3, 1998, p. 158 (in Russian).