ISSN 2455-4863 (Online) **www.ijisset.org** *Volume: 5 Issue: 3 | 2019*

Lattice Periodicity of Diamond Crystals and Related Phases

Andrzej Badzian

Materials Research Institute, the Pennsylvania State University,
N003 Millenium Science Complex, University Park , PA 16802, USA

Abstract: *The distribution of atoms in a crystal lattice is the primary goal of crystals characterization. Variety of X-ray diffraction methods provides the tools to determine the disturbance of lattice periodicity in single crystals. This report considers the justification for continuation of research on hydrothermal growth of diamond, the existence of hexagonal diamond phase and ordering in solid solutions of diamond and cubic boron nitride.*

The new invention in X-ray detectors based on the concept of charge-coupled detector established an easy way to check the periodicity of crystal lattice. According to Fourier transforms sharp diffraction peaks correspond to the periodic lattice of crystal.In the particular case of microwave plasma CVD (001) diamond single crystals one can register the additional X-ray scattering in the vicinity of reciprocal lattice points as pixel pattern shown in[1]. Compared with the scattering from nearly perfect natural diamond and electronic grade single crystal silicon indicates that additional scattering appears in CVD images. The standard diffraction patterns for scattering around reciprocal lattice point 111 for natural diamond is shown in Fig. 2A and 2B from reference [2] as 111 Bragg reflection. Bragg reflection for Si is shown in Fig. 1A and 1B of [2]. The scattering demonstrated in Figures 1-5 in reference [1] comes from displaced atoms from perfect lattice, disturbing periodicity. These pixel images data were obtained with RIGAKU D/MAX Rapid IIX-ray diffractometer.

The data for lattice periodicity of CVD diamonds are scarce. Till now two polytypes of diamond were noticed by x-ray diffraction. One with the triple diamond periodicity and other one with double 111 interplanar spacing. [2]

It would also be ofinterestto find out about thegrowth defects of HP/HT diamond single crystals grown as isotopically pure crystals of high thermal conductivity at GE laboratory. [3] The curiosity extends tothe acetylene-oxygen flame torch crystals. [4] HP/HT diamond grit crystals preserve long range order despite inclusions of catalyst-solvent carbides inclusions. [5]

Fig. 2 in [2] represents nearly perfect natural diamond. It seems that these crystals should be mimicked to get diamond crystals of high grade lattice periodicity of long range order, but we do not know which growth process should be mimicked. Decades ago it was believed that the hydrothermal growth, in quartz, is worth to try. Several diamond trials, with different chemistries were performed, yielding single papers like [6]. A large research trust would be necessary to gain any progress because the need of a new concept of solution chemistry and sophisticated autoclaves.

Achieving good lattice periodicity is of critical importance for structural characterization of single crystal of hexagonal diamond.The first experiment on HP/HT transition from single crystal graphite from Madagascar to hexagonal diamond conducted by Bundy and Kasper at GE laboratories in 1967 followed well-chosen concept of HP process.[7] The transition did not create one large single crystal of hexagonal diamond. Instead a polycrystalline material emerged with larger crystallites of hexagonal diamond.The determination of hexagonal phase took place for larger crystallites considered as small single crystal.These are the limits at which hexagonal phase was confirmed. The accuracy of lattice parameters was low, 0.02Å.

The X-ray diffraction precession method allowed identification of hexagonal diamond structure of such crystallites. The precession camera produces an undisturbed picture of the reciprocal lattice of an illuminated single crystal. This way the real symmetry of crystal hexagonal lattice was observed. The difference between cubic and hexagonal diamond is clearly caught in the precession pictures. It is stated on page 3443 of reference [7]: “formation of larger crystallites of hexagonal diamond could be identified and compared to the orientation of starting graphite crystal.” And further: “The direct examination of reciprocal space with the precession technique reveled clearly not only hexagonal symmetry of the new phase but also that the crystals were twinned and in special and unanticipated epitaxial relationship to the original graphite crystal.”

The spots on the precession image are larger and rounded. It is to be considered if it can be connected to the mosaic spread of crystal blocks or displacement of atoms in the lattice. TEM is necessary, but the sample is lost according to Dr. Robert DeVries. No macroscopic samples are available now.

For smaller crystallites material X-ray Debye-Scherrer pattern clearly showed hexagonal diamond Miller indexes in contrast to cubic diamond. Long range order of hexagonal diamond lattice is proven, but confusion exists in literature about the existence of crystal lattice of hexagonal diamond. In general papers report on materials with dense planar disorder. The answer to

the present problems is easy: reproduce Bundy & Kasper experiment. Since 1967 nobody reproduced HP experiment with graphite single crystal in the manner of Bundy &Kasper. Elucidation of the existence of hexagonal diamond phase is an important scientific task.

What should be considered in new experiments is the heating graphite single crystal. Should flash heating be improved? GE experiments, produce a difficult to control environment in comparison to more stable heater like described in report about transition in hexagonal boron nitride-graphite solid solutions. [8] These materials possess an intermediate electric resistivity between insulator hexagonal boron nitride and semi metal graphite $(BN)_x(C_2)_{1-x}$, where $0<x<1$.[9] Aside the study of the phase transition, theinteresting materials have been synthetized using proper heater for HP/HT transitions. Making a capsule from graphitic type material and placing graphite single crystal inside the HP vessel can be worth to try. It can be Bridgeman anvils, hemispherical anvils or a high compression belt apparatus. It will be necessary to test if BN-C will be practical in HP chamber where material inside moves when the squeezingtakes place before HP run starts. Then the resistivity of graphitic type heater can be adjusted according to chemical composition parameter x in the formula above, and high temperature easily achieved by passing current.

The CVD process was applied to synthetize graphite-hexagonal BN solid solutions from the mixture ofCCl_4 , BCl_3 , N_2 and H_2 gases . Radio- frequency generator of frequency 3-4 MHz and power of 20 kW was used to heat graphite susceptor in tubular systemto 1900^0 C where the BN-C deposition took place.[9] At lower temperatures B_4C appeared. This is the right temperature to deposit solid solutions. The sign that the ordering of BNC layers appearsarehkl x-ray reflections responsible for layer ordering sequence. A prominent 112 line was recorded.Turbostratic disorder limits reflections to 00l and hk0. Such materials qualify as a good heater for harsh chemical environment as well as for HP chambers.

The transition in graphitic solid solution type $(BN)_x(C_2)_{1-x}$, where $0<x<1$, phases took place at 14 GPa and temperatures 3000^0 C resulting in solid solution of diamond and cubic boron nitride. [8,10] These cubic crystal phases show long range order. Debye- Scherrer pattern counts 20hkl reflections up to 0.40 Å. If diffraction data come from deep reciprocal space region (it means for higher order hkl), we can receive more detailed data for short distances in the real space.The cubic diamond phase created at such extreme conditions preserved exceptional lattice periodicity. Also B atoms occupy one of face center cubic sublattices and N atoms the other.

In conclusion, the new generation of x-ray detectors provides a promising tool for more detailed inspection into the reciprocal space of diamond family of materials, giving more detailed knowledge about the disturbance of diamond lattice periodicity.

Acknowledgements

This report was supported by Penn State Materials Research Institute grant # UP31200.

References

[1] A. Badzian, The X-Ray Diffraction Method for Study of Growth Defects in CVD Diamond Single Crystals, Advances in Materials 7(4) (2018) 89-104

[2] A.Badzian, The displacement disorder of atoms in diamond crystals revealed by x-ray imaging plate detector, Diamond and Related Materials 69, (2016), 19-32.

[3] L. Wei, P.K.Kuo, R.L. Thomas, T.R. Anthony and W. F. Banholzer, Thermal Conductivity of Isotopically Modified Single Crystal Diamond, Phy. Rev. Lett. 70(24) 1993, 3764-3767

[4] K. Hirabayashi and Y. Hirose, Synthesis and Growth Mechanism of Flattened Diamond Crystals, Diamond and Related Materials, 5 (1996) 48-52

[5] A. Badzian and A. Klokocki, On the Catalitic Growth of High Pressure Diamonds, J. of Crystal Growth, 52 (1981) 843-847

[6] X-Z.Zhao, R. Roy, K. Cherian, and A. Badzian, Hydrothermal Growth of Diamond in Metal –C-H_2O System, Nature 1997 (385) 513-515

[7] F. P. Bundyand J.S. Kasper, Hexagonal Diamond-Anew Form of Carbon, J. of Chem. Phys. , 46 (1967) 3437-3445

[8] A.Badzian, Cubic Boron Nitride –Diamond Mixed Crystals (Solid Solution), Mat. Res. Bull. 16 (1981) 1385-1393

[9] A.Badzian, T Niemyski, S. Appenheimer, E. Olkusnik, "Graphite-Boron Nitride Solid Solutions" in F.A. Glaski, (Ed.), Proceedings of the Third International Conference on Chemical Vapor Deposition, Salt Lake City, April 24-27, 1972, American Nuclear Society

[10] A. Badzian, Defect structure of Synthetic Diamond and Related Phases, Advances in X-Ray Analysis eds. Charles S. Barrett, John V. Gilfrich, Ron Jenkins, John C. Russ, James W. RichardsonJr. and Paul K. Predecki Vol. 31, 113-128, Plenum Publishing Corporation, 1988