Ceramics International **22** (1996) 223–228
©1996 Elsevier Science Limited and Techna S.r.l.
Printed in Great Britain. All rights reserved
0272-8842/96/$15.00

0272-8842(95)00092-5

Defects in CVD diamonds

Andrzej Badzian & Teresa Badzian

Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA

(Received 10 July 1995; accepted 1 August 1995)

Abstract: Crystallographically perfect diamond films and crystals can be grown by microwave-assisted CVD processes. The degree of quality of these crystals depends on the growth sector and process parameters. Surface reactions in the presence of atomic hydrogen can initiate the formation of twins and stacking faults. These defects disturb the stacking sequence of tetrahedra necessary for cubic diamond structure. X-ray techniques were used to determine disturbance of diamond lattice periodicity. Planar and linear disorders were analyzed with the help of X-ray diffuse scattering. The diffuse scattering around (111) reciprocal lattice point can be used as a test for crystallographical perfection of diamond crystals.

1 INTRODUCTION

Crystals grown by chemical vapor deposition methods are usually twinned. Methods of eliminating twinning in boron and boron carbide crystals are difficult to attain. Boron carbide crystals grown from a radio frequency plasma ignited in a BCl_3, CCl_4 and H_2 mixture, form aggregates of micro-twin domains with a wide-angle spread. Single crystals of ß-rombohedral boron ($\bar{m}$ point group) did not reveal a three-fold axis of symmetry in the $<0001>$ direction, as determined by an X-ray Laue photograph. ß-rombohedral boron has a complicated crystal structure with 105 atoms in the rombohedral unit cell. Boron atoms are arranged in an icosahedral network. A structural subunit is composed of 84 atoms inside a sphere with the spheres forming a rombohedral lattice. This lattice has a close relationship to a face-centered cubic lattice, which forms twins. The lack of a three-fold axis of symmetry, assuming microtwinning on the $\{2021\}$ planes,[1] may have resulted in quasi-crystalline lattice of elemental boron. Other researchers later introduced the name 'quasicrystals' for metal alloys.

Crystals with less complicated atomic structures, such as silicon (derived from an fcc lattice), are twinned when grown by CVD. Pioneers of CVD diamond growth reported the same twinned forms as for Si: icosahedral forms[2] and pentagonal forms showing a 7° angle mismatch.[3]

Despite a general tendency toward twinning in CVD environments, we anticipated that in the case of CVD diamonds we would control this (in our case) undesirable phenomenon and therefore avoid the twinning typical of B_4C.

Our goal is to grow nearly perfect single crystal diamonds where carbon atoms form a strictly periodic array. Undesired scattering of phonons or charged carriers is minimized, yielding a high thermal conductivity material or semiconductor.

In this paper we report on an X-ray diffraction study of homoepitaxial films of diamond focused on evaluation of lattice periodicity and the determination of displacement disorder of the atoms.

2 SINGLE CRYSTAL GROWTH

An important task of diamond growth experiments from the gas phase is testing the feasibility of obtaining large single-crystal diamonds by new methods. Two methods are currently used: flame[4,5] and microwave plasma.[6]

Our crystal growth experiments were conducted with tubular microwave plasma CVD reactor.[7] Feed gases were CH_4 and H_2, and small amounts of B_2H_6, O_2 and N_2 were added during some processes. Natural diamond substrates (types Ia and IIa crystals) and high pressure/high temperature (HP/HT) Sumitomo crystals were used. Growth in the <001>, <110> and <111> directions were studied. Single crystal films up to 250 μm thick and a single crystal prism 1.2 mm high were grown.[8–10] Thin boron-doped films were used to fabricate electronic devices.[11]

3 X-RAY DIFFRACTION EXPERIMENTS

CVD diamond films on diamond substrates were investigated by Laue, oscillation and rotation methods. Laue photographs, using copper radiation and a cylindrical camera (57 mm and 114 mm in diameter), were taken. Oscillation and rotation photographs were taken with the same camera. Because of the low X-ray absorption coefficient of carbon, CVD films and diamond substrates were analyzed by scattering from both parts of the same sample simultaneously. These experiments provided clear evidence of which films were single-crystal and which were not.

The definition of single-crystal requires atoms being located along straight lines with a specific repetition distance. These lines span opposite sides of a single crystal. X-ray diffraction techniques allow repetition distance measurements of atoms for crystallographic directions consistent with a diamond unit cell. References on X-ray crystallography detail this approach.

Laue photographs of single crystals of natural or HP/HT diamonds show reflections originated by white radiation. On rotation photographs these crystals give sharp reflections on parallel levels. The distances between the levels allow calculation of the repetition distance of atoms lying on the line parallel to the axis of crystal rotation.

CVD epitaxial films were tested according to these criteria. Several films met the criteria of a single crystal epitaxial film and comparison with the substrate showed almost no difference in X-ray scattering. Other characterization methods also confirmed the high quality of these films.[9,10]

Films were grown on the (001) substrate at 875°C and on (110) substrates at 1100°C. These, results indicate that it is possible to find, despite the tendency to twin, conditions for the growth of nearly perfect crystals. However this search is based on the general rules of crystal growth and on a trial and error approach. Understanding of diamond growth processes is not sufficiently advanced to make accurate predictions, and we do not know why lattice distortions are so frequently observed when the growth conditions are changed.

Figure 1 shows a Laue pattern of CVD diamond film with lattice distortions. The differences in a Laue pattern from a nearly perfect crystal are as follows:

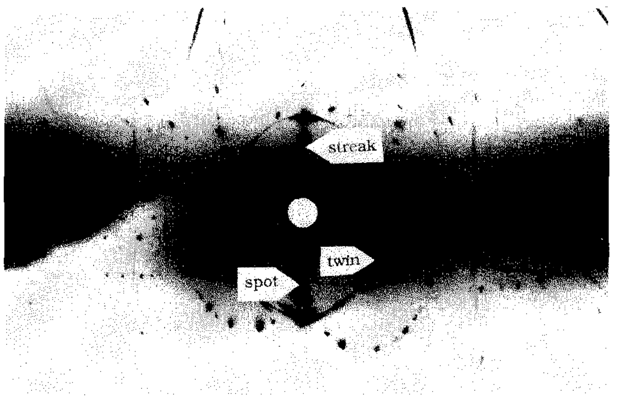

Fig. 1. Laue photograph of 80 μm diamond film on (001) type IIa natural diamond taken with CuKα radiation in a cylindrical camera. The film was covered by Ni foil. The primary beam was parallel to the <111> direction. The film was grown from 1% CH_4 in H_2 at 950°C and 70 Torr.

1. Reflections are elongated, indicating misoriented crystalline domains, as for a mosaic structure.
2. Microtwinning. The reflections indicated on Fig. 1 correspond to twinned domains.
3. Streaks correspond to planar defects.
4. Spots correspond to linear defects.

The features seen on the Laue photographs located outside the reciprocal lattice points indicate a disturbance in the lattice periodicity. The following section will justify this statement using some elements of kinematical theory of X-ray diffraction.

4 DIFFRACTION EFFECTS OF LATTICE DEFECTS

The kinematical theory of X-ray diffraction in crystals is based on the autocorrelation theorem of Fourier transform.[12–15]

If $\rho(\bar{r})$, the electron density function of a crystal, has the Fourier transform F(s) (known as structural amplitude)

$$F(\bar{s}) = \int \rho(\bar{r})\exp(-2\pi i \bar{r}\bar{s})\mathrm{d}Vr,$$

then its autocorrelation function

$$Q(\bar{r}) = \int \rho * (\bar{y})\rho(\bar{r}+\bar{y})\mathrm{d}V_y$$

has the Fourier transform $|F(\bar{s})|^2$, where $\bar{r}$ is the vector in real space, $\bar{s}$ is the vector in reciprocal space, and $\bar{y}$ is the vector related to a point in real space taking part during integration.

For an ideally periodic lattice, the structural amplitude is expressed by

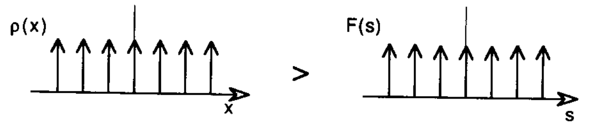

Fig. 2. One-dimensional lattice and its Fourier transform.

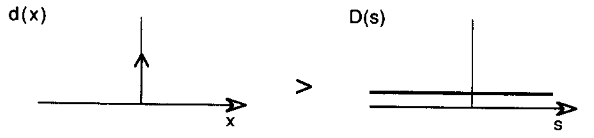

Fig. 3. A point defect expressed by impulse function and its Fourier transform.

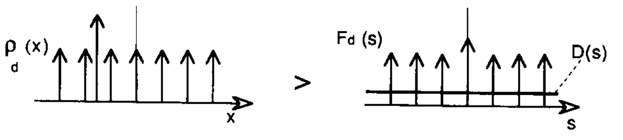

Fig. 4. One-dimensional lattice disturbed by interstitial atom and its Fourier transform.

$$F_{hkl} = \sum_i f_i(\bar{s})\exp\{-2\pi i(hx_i + ky_i + lz_i)\}$$

where the sum takes place for atoms inside the unit cell. The atomic coordinates are x_i, y_i and z_i. I(s) is the experimental intensity function, which describes the distribution of intensity of scattered X-ray in reciprocal space and is expressed by the equation

$$I(\bar{s}) = \alpha \mid F(\bar{s}) \mid^2$$

where α is a combined scaling factor taking into account the conditions of the experiment.

We represent atoms as point-like scattering centers arranged according to a periodic lattice. Figure 2 shows the structural amplitude. Reference 12 explains the representation of these functions, as shown in Fig. 2.

If atoms take those positions along the periodic lattice, the intensity is concentrated at the reciprocal lattice points, the arrows correspond to Bragg reflections and the function is zero between reciprocal lattice points.

Let us consider the function $\rho_d(x)$ whose periodicity is disturbed by a vacancy or an interstitial atom (Fig. 3). The defect can be represented by the impulse d(x) symbol.[12] The Fourier transform of an impulse is a constant function in reciprocal space.

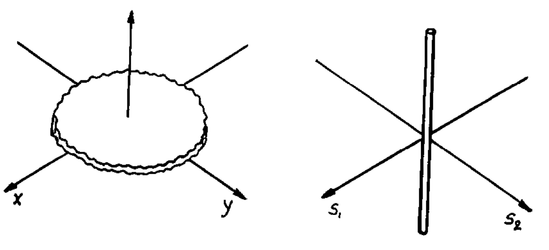

Fig. 5. Two-dimensional Fourier transform of a shape function of a planar defect.

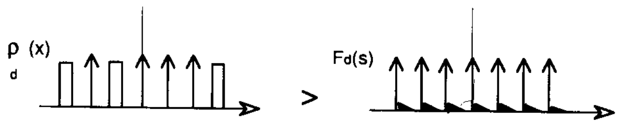

Fig. 6. A schematic representation of lattice with planar defects. The planar defects are shown as rectangular functions. The coordinate X is perpendicular to the plane of the defect. The diffraction pattern has streaks associated with the reciprocal lattice points.

The electron density function $\rho_d(x)$ of a lattice with a defect is described by a sum of the periodic function $\rho(x)$ and a function describing the defect d(x). The addition theorem is applied to the sum function. If $\rho(x)$ and d(x) have Fourier transforms F(s) and D(s), respectively, then $\rho(x) + \mathrm{d}(x)$ has the Fourier transform $F(\mathrm{s}) + D(\mathrm{s})$.

The function D(s) is known as diffuse scattering and is a measure of the disturbance of the lattice periodicity. Diffuse scattering appears as a continuous background. When the density of vacancies of interstitial atoms increases and defects agglomerate the diffuse scattering has maximum at $s = 0$ (Fig. 4).

Now let us consider a planar defect in a three-dimensional lattice. An example of such a defect is a hexagonal stacking fault on the (111) plane of cubic diamond or the (111) twin. These defects introduce carbon atoms in the new lattice positions close to the defect plane. The description of such defects also includes a shape function that determines the boundaries of the defect. The shape function of a planar defect is similar to a flat object. The Fourier transform of a flat object in real space is an elongated object in reciprocal space, as shown in Fig. 5.

Hence an X-ray diffraction pattern of the elongated object in reciprocal space will correspond to a streak of X-ray intensity perpendicular to the planar defect.

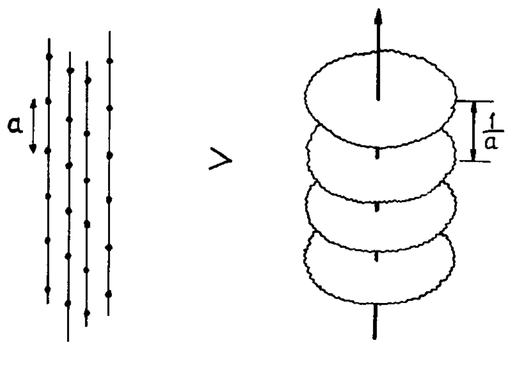

Fig. 7. A schematic representation of linear defects.

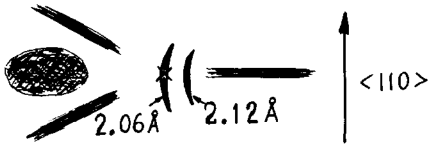

Fig. 8. X-ray scattering around the 111 reciprocal lattice point. Epitaxial film 100 μm thick was set to the Bragg reflection for CuKα line.

When planar defects are superimposed on a periodic lattice the diffraction pattern will contain streaks associated with the reciprocal lattice points, as shown in Fig. 6.

In addition to planar disorder in the diamond lattice, a linear disorder is also visible. The description of a pure case of linear disorder is as follows. Atoms are located on straight lines with strict periodicity, but the lines are shifted at random. The crystal lattice is periodic in only one dimension, as shown in Fig. 7. The X-ray intensity is concentrated on planes associated with the reciprocal lattice points. This is a reverse case of planar disorder shown in Fig. 5.

Planar and linear disorders appear in CVD diamond films, indicating that displacement disorder of atoms is more complicated than the models shown in Figs 6 and 7 suggest. Diffuse scattering around the 111 reciprocal lattice point demonstrate this situation, as shown in Fig. 8.

5 DISCUSSION

X-ray diffuse scattering provides a convenient method for analysis of the disturbance lattice periodicity in crystals. If a given lattice is strictly periodic diffuse scattering should not be seen. Maximum diffuse scattering is associated with the 111 reciprocal lattice point (see Fig. 8) for CVD diamonds and can be used as a test of lattice perfection.

We have three objectives in our study of defects in diamond crystals:

1. defect identification,
2. examining the relationship of defect formation to growth parameters and chemical environments, and
3. discovering the cause of defect formation.

Study of defects in CVD diamond crystals is at a preliminary stage. However, some aspects are discussed below.

5.1 Twinning

When diamond nucleates on non-diamond substrates, it is frequently observed that neighbor crystals have drastically different morphologies. For example, a cubooctahedral crystal grew next to densely twinned agglomerate (Fig. 9). The (001) homoepitaxy is disturbed by hillock formation, which originates in twinning.

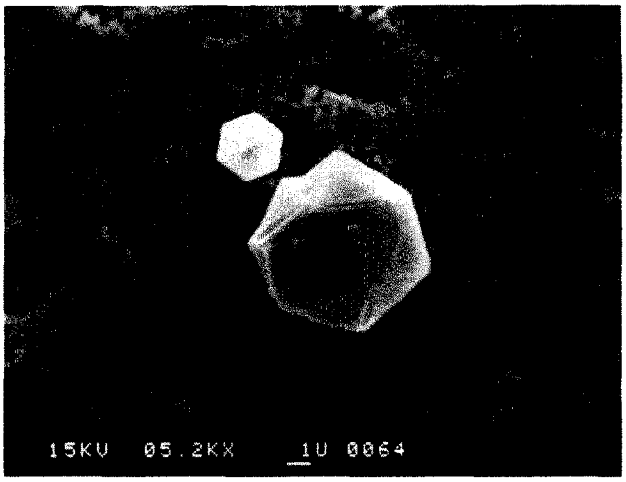

Fig. 9. Two diamond crystals grown on silica substrate.

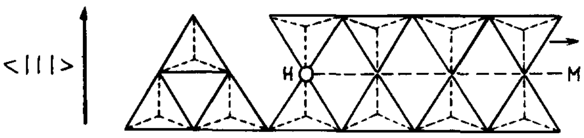

Fig. 10. Anticipated formation of the (111) twin.

Our hypothesis concerning the cause of twinning is explained in Fig. 10. As diamonds grow on the (111) surface, a hydrogen atom is incorporated at the top of a tetrahedron. This event causes the tetrahedron in the next layer to be reversed, and the growth of a twin continues. It is anticipated that tetrahedrons on the opposite side of the mirror plane will be deformed, since tetrahedra configuration in space are completely different from the cubic diamond structure. Thus, impurity atoms like H, Si and Ti incorporated into a diamond lattice may initiate twinning.

5.2 Stacking faults

Diamond belongs to the group of tetrahedral structures. It exists as cubic and hexagonal allotropes, but can also form polytypes. A superstructure with three times longer periodicity than cubic diamond was assigned to a newly found stacking sequence.[9,10] Growth conditions of this form suggest that active participation of nitrogen in surface reactions might influence stacking of tetrahedra in the <111> direction. An independent study on CVD diamonds indicated stacking faults and twinning in lattice images by high resolution TEM.[16,17]

Our working hypothesis is that deformation of tetrahedra takes place when stacking departs from cubic ABCABC type stacking. This deformation causes an elongation of the tetrahedron so that the height increases from 2.06 to 2.12 Å. Figure 8 shows that the satellite Bragg reflection corresponding to interplanar spacing of 2.12 Å is related to tetrahedra deformation.

If the hypothesis is correct, it would mean that sp^3 hybridization of carbon atoms is not as symmetric as in cubic diamond.

It is common for CVD diamond to show mixed characteristics of cubic diamond and forms of tetrahedral carbon. This is an indication that proper stacking of the new form coexists with cubic diamond stacking and as a result introduces displacement disorder of carbon atoms.

We prepared the new form of tetrahedral carbon in a pure form by (111) epitaxy. This form shows the satellite Bragg reflection (Fig. 8), and the Raman peak at 1332 cm^{-1} is seen to be completely absent.

5.3 sp^2 type defects

Co-nucleation of diamond and graphite was a critical issue during the early stages of development of CVD methods. Graphite co-deposition was an obstacle to successful diamond growth. Advances in the CVD deposition of diamond were accompanied by increasing the concentration of atomic hydrogen in the plasma. When appropriate concentrations of H° were achieved, the issue of graphitic co-deposition lost its previous importance.

Graphitic inclusions inside diamond crystals were rarely observed. Nanocrystals of graphite 30×50 Å with the basal plane at graphite parallel to the (111) plane of diamond were detected by TEM.[18] We have also proposed a single plane of graphite inserted between two (111) planes of diamond.[19]

Recent observations of CVD diamonds with high-resolution TEM were not able to detect graphitic inclusions; however, twins were observed.[20,21]

Modification of the bonding network can be seen in changes introduced by twinning, rather than by a 'graphitic component'. This component was never clearly described as a particular configuration of carbon atoms.

5.4 Vacancies

Our study indicates that neutral vacancies formed during growth are rarely observed in CVD crystals. The neutral vacancies were detected with luminescence experiments in the <111> growth sector.[22] In contrast, a peak is frequently observed in photoluminescence, which is shifted relative to the GR-1 peak. This peak is not affected by annealing of samples up to 1200°C. Most often, we assign this peak to silicon atom-vacancy complex. This peak appears in silicon doped epitaxial diamond films grown at 1200°C.[23]

6 CONCLUSIONS

The main conclusion from this study is a reverse picture of 'defects' in CVD diamond. The sp^2 component is of negligible importance in growth environments rich in atomic hydrogen when compared to stacking faults and twinning. CVD diamonds can be grown as nearly perfect diamond crystals, as well as films of different forms of tetrahedral carbon. These tetrahedral forms are different from cubic and hexagonal diamond, in the sense that they possess a different degree of stacking order. X-ray diffuse scattering was used to detect disturbances of lattice periodicity, and we found that the scattering associated with the 111 reciprocal lattice point is a reliable test for crystallographic perfection of CVD diamonds.

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation under grant no. DMR9522566 and by the Office of Naval Research with funding from BMDO under grant no. 00014-95-I-0905.

REFERENCES

1. BADZIAN, A., KLOKOCKI, A. & NIEMYSKI, T., *Electron Technol.*, **3** (1970) 143.
2. SPITSYN, B. V., BOUILOV, L. L. & DERJAGUIN, B. V., *J. Cryst. Growth*, **52** (1981) 219.
3. MATSUMOTO, S. & MATSUI, Y., *J. Mater. Sci.*, **18** (1983) 1785.
4. JANSSEN, G., VAN ENCKEVORT, W. J. P., SCHAMINEE, J. J. D., VOLLENBERG, W., GILING, L. J. & SEAL, M., *J. Cryst. Growth*, **104** (1990) 752.
5. SNAIL, K. A. & HANSSEN, L. M., *J. Cryst. Growth*, **112** (1991) 651.
6. KAMO, M., YURIMOTO, M. & SATO, Y., *Appl. Surf. Sci.*, **33/34** (1988) 553.
7. KAMO, M., SATO, Y., MATSUMOTO, S. & SETAKA, N., *J. Cryst. Growth*, **62** (1983) 642.
8. BADZIAN, A., BADZIAN, T. & PILIONE, L., *Int. J. Refact. Metals Hard Metals*, **9** (1990) 92.
9. BADZIAN, A., BADZIAN, T., WANG, X. H. & HARTNETT, T. M., In *New Diamond Science and Technology*, ed. R. Messier, J. T. Glass, J. Butler and R. Roy. Materials Research Society, Pittsburgh, PA, 1991, p. 549.

10. BADZIAN, A. & BADZIAN, T., *Diamond Relat. Mater.*, **2** (1993) 147.
11. GILDENBLAT, SH. G., GROT, S. A. & BADZIAN, A., *Proc. IEEE,* **79** (1991) 647.
12. BRACEWELL, R., *The Fourier Transform and its Applications*. McGraw-Hill, New York, 1965.
13. HOSEMANN, R. & BAGCHI, S. V., *Direct Analysis of Diffraction by Matter*. North Holland, Amsterdam, 1962.
14. GUINIER, A., *Theorie et Technique de la Radiocristallographie*. Dunod, Paris, 1956. .
15. WOOSTER, W. A., *Diffuse X-Ray Reflections from Crystals*. Clarendon Press, Oxford, 1962.
16. WILLIAMS, B. E., GLASS, J. T., DAVIS, R. F., KOBASHI, K. & MORE, K. L., In *Science and Technology of New Diamond*, ed. S. Saito, O. Fukunaga and M. Yoshikawa. KTK Scientific Publishers, Tokyo, 1990, p. 319.
17. ETO, H., TAMOU, Y., OHSAWA, Y. & KIKUCHI, N., *Diamond Relat. Mater.*, **1** (1992) 373.
18. ZHU, W., RANDALL, C. A., BADZIAN, A. & MESSIER, R., *J. Vac. Sci. Tech.*, **A7** (1989) 2315.
19. BADZIAN, A., In *Advances In X-Ray Analysis*, ed. C. S. Barrett. Plenum Press, New York, 1988, vol. 31, p. 113.
20. KIKUCHI, N., OHSAWA, Y., TAMOU, YU., ETO, H. & YAMASHITA, H., In *New Diamond Science and Technology*, ed. R. Messier, J. T. Glass, J. Butler and R. Roy. Materials Research Society, Pittsburgh, PA, 1991, p. 567.
21. SHECHTAMN, D., FELDMAN, A., VAUDIN, M. D. & HUTCHISON, J. L., *Appl. Phys. Lett.*, **62** (1993) 487.
22. YACOBI, B. G., BADZIAN, A. R. & BADZIAN, T., *J. Appl. Phys.*, **69** (1991) 1643.
23. YACOBI, B., LEBENS, J., VAHALA, K. J., BADZIAN, A. & BADZIAN, T., *Diamond Relat. Mater.*, **2** (1993) 92.