ISSN 1027-5495. Functional Materials, 23, No.4 (2016), p. 552-556.
doi:https://doi.org/10.15407/fm23.04.552 © 2016 — STC "Institute for Single Crystals"

Change of dislocations density in single crystals of various types diamonds depending on the growth temperature and rate

O.M.Suprun[1], G.D.Il'nitskaya[1], V.A.Kalenchuk[1], O.A.Zanevskii[1], S.N.Shevchuk[2], V.V.Lysakovskii[1]

[1]V.Bakul Institute for Superhard Materials, National Academy of Sciences of Ukraine, 2 Avtozavods'ka Str., 04074 Kyiv, Ukraine
[2]SedKrist GmbH, Ebereschenring 14, 14554 Seddiner See, Germany

Received April 28, 2016

Single crystals of various types of diamonds have been grown by the melt solution crystallization at high pressures and temperatures. To define the emergences of dislocations onto the {100} and {111} faces, the selective etching of the crystals in KOH and KNO_3 melt has been used. It has been defined that the dislocation density, N_d, in diamond single crystals grown at a low growth rate of 1–2 mg/h at T = 1420–1500°C is $0.8–3{\cdot}10^2$ cm^{-2} and the dislocation densities, N_d, in single crystals grown at temperatures 1280–1450°C and 1280–1350°C at growth rates of 3–5 mg/h and 20–25 mg/h are $1.1–2.2{\cdot}10^3$ and $1.06–1.35{\cdot}10^6$ cm^{-2}, respectively.
Keywords: diamond single crystals, dislocations density, selective etching, etching pits.

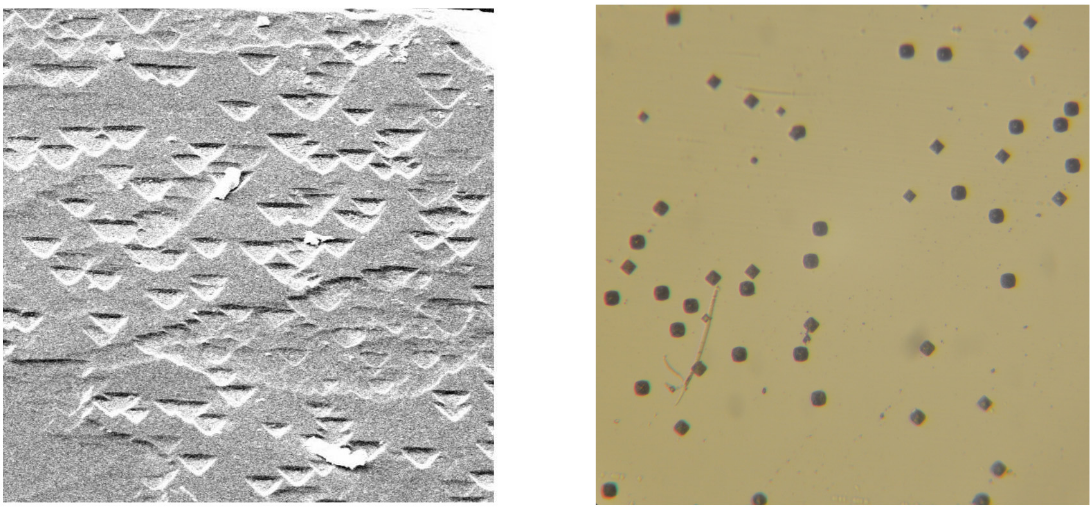
Монокристаллы алмаза различных типов выращены методом раствор-расплавной кристаллизации при высоких давлениях и температурах. Для определения выходов дислокаций на грани {100} и {111} применен метод избирательного травления кристаллов в расплаве KOH и KNO_3. Показано, что плотность дислокаций $N_Д$ составляет $0{,}8\div3{\cdot}10^2$ см$^{-2}$ для монокристаллов алмаза, выращенных при низких скоростях роста, 1–2 мг/час, при T = 1420–1500°С. Для скоростей выращивания 3–5 мг/час и 20–25 мг/час при температурах 1280–1450°С и 1280–1350°С, соответственно, величина $N_Д$ определена $1{,}1\div2{,}2{\cdot}10^3$ и $1{,}06\div1{,}35{\cdot}10^6$ см$^{-2}$.

Зміна густини дислокацій монокристалів алмазу різних типів в залежності від температури вирощування і швидкості росту. *О.М.Супрун, Г.Д.Ільницька, В.А.Каленчук, О.О.Заневський, С.М.Шевчук, В.В.Лисаковський.*

Монокристали алмазу різних типів отримано методом розчин-розплавної кристалізації при високому тиску і температурах. Для визначення виходів дислокацій на грані {100} і {111} застосовано метод вибіркового травлення кристалів в розплаві KOH і KNO_3. Показано, що густина дислокацій $N_Д$ становить $0{,}8\div3{\cdot}10^2$ см$^{-2}$ для монокристалів алмазу, вирощених при низьких швидкостях росту, 1–2 мг/год, при T = 1420–1500°С. Для швидкостей вирощування 3–5 мг/год і 20–25 мг/год при температурах 1280–1450°С і 1280–1350°С, відповідно, величину $N_Д$ визначено $1{,}1\div2{,}2{\cdot}10^3$ і $1{,}06\div1{,}35{\cdot}10^6$ см$^{-2}$.

1. Introduction

The results of the investigations into strength properties of solids performed with the use of calculated models, based on the solids crystal structure, differ from the real data obtained by testing [1]. These differences appear because the existence of the crystal lattice defects, first of all, dislocations, which are not allowed for in the cal-



a) b)

Fig. 1. Etching pits typical for diamond faces (500× magnification): trigonal for {111} (a); tetragonal for {100} (b).

culations. As it turns out, dislocations are very stable defects and may essentially affect the crystals properties, mainly mechanical [2].

To observe and detect the dislocations in diamond single crystals, a selective etching method was developed [3, 4]. It is found that in etching of single crystals on their faces there form faceted pits of the corresponding symmetry, which are connected with the sites of dislocations emergence [5, 6]. In etching the faces of the defective crystals dissolve better than those more structurally perfect. As a result of the dissolution there form the etching pits located more or less randomly on a crystal faces.

The advantages of the selective etching are the simplicity and rapidity of the application, which allows one to define and study the density and distribution of dislocations within various single crystals [7–14] as well as to assess the crystals quality [15]. The data obtained using the selective etching rather well correlate with the results obtained by other methods, e.g., when using X-ray topography [16]. The methods of detecting the dislocations by selective etching are widely used for various types of crystals, but for diamond there is a problem of searching a suitable composition of the etchant [5, 17].

The aim of the present study was to choose the optimal conditions of the selective etching of diamond single crystals, to define the etchability of faces, types and shapes of the etching pits in order to define the dislocations density in diamond crystals and its variation depending on the growth temperature and rate.

2. Experimental

For studying we used types Ib, IIa, and IIb diamond single crystals of sizes 3–7 mm of cubooctahedral and cubic habits (the crystals were grown by the temperature gradient method [18, 19] at the rates of 1–2 and 3–5 mg/h) and spontaneous crystals of size 1.2–2 mm with a cubooctahedral habit, grown at the rate of 20–25 mg/h. All crystals were with smooth faces, optically transparent, and without visible inclusions at microscope magnification of 56×.

To apply the selective etching, we tested and used various etchants, but the most effective was the composition of mixture of potassium hydroxide (KOH) and niter (KNO_3) in the ratio of 3:1, which is widely used to clean the surfaces in producing diamond grinding powders. The crystals etching was performed in a muffle furnace at the temperature of 550±10°C–660±10°C and ambient pressure, the time varied from 10 to 30 min. On etching the crystals were thoroughly washed with distilled water and ethyl alcohol.

The selective etching of samples produced by the temperature gradient was started at 550–580°C and holding time from 10 to 30 min, then the temperature was increased to 650–660°C and time from 30 to 60 min. Under these conditions the emergence of dislocations appears as etching pits on the crystals faces. The shape of the pits

Table 1. Dislocations density in various types diamond crystals seed-grown by temperature gradient in the thermodynamic stability region at pressure of 6–6.2 GPa, temperature of 1420–1500°C, and growth rate 1–2 mg/h

Type of crystals	Growing temperature, °C	Growth system	Dislocations density N_d, cm^{-2} on the {100} faces	Amount of crystals used for the calculation
Ib	1420÷1450	Fe–Ni–Co	$0.8 \div 1.8 \cdot 10^2$	6
IIa	1450÷1500	Fe–Al–Zr	$1.5 \div 2.1 \cdot 10^2$	6
IIb	1450÷1500	Fe–Al–B	$1.9 \div 3 \cdot 10^2$	6

Table 2. Dislocations densities in diamond crystals seed-grown by temperature gradient in the thermodynamic stability region at temperatures 1280–1450°C and growth rates 3.5–5.0 mg/h

Type of crystals	Growth temperature, °C	Growth system	Dislocation density, cm^{-2} on the {100} faces	Amount of crystals used in calculations
Ib	1280–1420	Fe–Ni–Co	$1.1–2.1 \cdot 10^3$	8
IIb	1420–1450	Fe–Al–B	$1.6–2.2 \cdot 10^3$	5

that form on the crystals faces coincides with orientation of the faces [5] (Fig. 1).

3. Results

Figure 2 shows the typical etching pits that appear on 100 faces of the type IIb diamond single crystals. The specific spatial arrangements of the dislocations in single crystals and their emergence on the corresponding faces of a cube and octahedron are defined by the value and direction of the Burgers vector $\bar{b}$ at the etching spot [6], therefore, the shapes and sizes of the pits are different (Fig. 2). An increase of the etching time to 60 min and above results not in increase of the etching pits number, but only in the increase of their sizes.

As is known [20], the dislocation density, N_d, may be calculated by the formula:

$$N_d = \frac{D_{av}}{M_s} \quad (1)$$

where D_{av} is an average number of the etching pits, M_s is the field area, cm^2.

Dislocations density, N_d, that we experimentally defined for 6 type IIb crystals grown at 1420–1480°C (Table 1) is $1.9–3 \cdot 10^2$ cm^{-2}, for other types of crystals these values are evaluated at $1.5–2.1 \cdot 10^2$ cm^{-2} (type IIa, 6 measurements) and $0.8–1.8 \cdot 10^2$cm^{-2} (type Ib, 6 measurements) (see Table 1).

As is seen from the data listed in Table 1, dislocations densities in different types crystals grown in the temperature range from 1420 to 1500°C differ little from one another. In this case we should note that 80 % of (100) and (111) faces have no emergence of the dislocations.

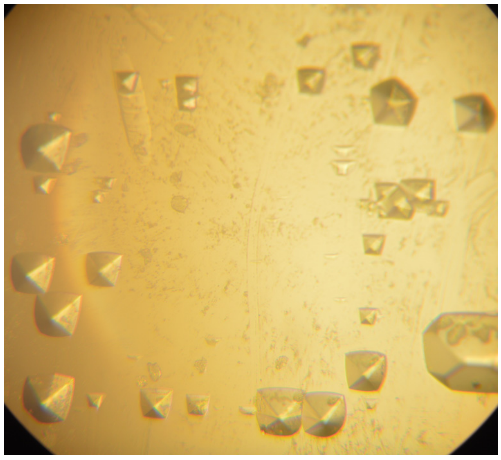


Fig. 2. Image of type IIb diamond crystal surface after 145 min of etching, (100) face, 200× magnification; the crystal was grown at p = 6.1 GPa and T = 1450–1500°C using a Fe–Al–B solvent, the dislocation density is evaluated at $3 \cdot 10^2$ cm^{-2}.

Of a special interest was the growing of types Ib and IIb diamond single crystals by temperature gradient at the low temperature, i.e., the use of low-temperature solvent based on the Fe–Ni alloy doped with special alloying additions, which makes it possible to grow structurally perfect single crystals of the cubic habit at the temperature of 1280–1450°C with the growth rate of 3.5–5 mg/h. The grown crystals exhibited the extent of the cube faces development to 90–95 %. We should note that un-

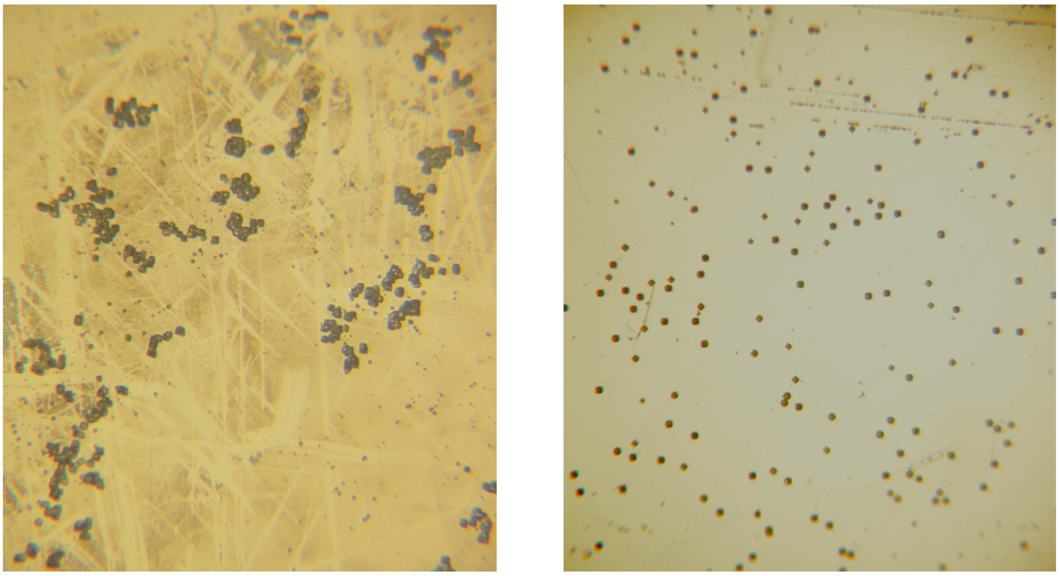


Fig. 3. Surfaces of diamond crystals after etching for 20 min: type Ib, face (100), crystals grown at 1280–1420°C (a); type IIb, face (100) grown at 1420–1450°C (b).

like the crystals grown at 1420–1500°C (see Table 1), the crystals of the cubic habit (Table 2) demonstrated the formation of the etching pits (Fig. 3) at much lower etching temperatures (550–560°C) and increasing the dislocations density approximately by a factor of 10.

We have also defined a change of the dislocation density in single crystals produced by the spontaneous recrystallization of graphite into diamond at the rate of ~20–25 mg/h. Fig. 4 shows the picture of etching on (111) face of the diamond sample grown by spontaneous crystallization at pressure of 5.8–6 GPa and temperature of 1280–1350°C the dislocation density was $1.06\text{–}1.35 \cdot 10^6$ cm^{-2}, the alloy-solvent was Fe–Co–Mn. After spontaneous crystallization the etching pits start to appear at 580°C; dislocations density was defined by Eq. (1) as the average of three crystals.

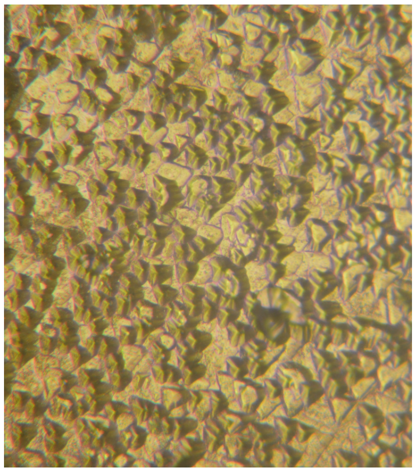


Fig. 4. Surface of a diamond crystal produced by spontaneous crystallization after etching for 20 min (the crystal of type Ib diamond is grown at $p = 5.8\text{–}6.0$ GPa and $T = 1280\text{–}1350$°C, growth rate was 20–25 mg/h), 200× magnification

4. Conclusions

Thys, our experiments give grounds to conclude that use of $KOH + KNO_3$ etcher for selective etching of diamond single crystals makes it possible at temperatures of 550–660°C to observe the picture of the emergence of dislocations onto the faces and define the dislocations density. In growing by the temperature gradient the dislocation densities of all types diamonds grown in the diamond thermodynamic stability region in the temperature range from 1450 to 1500°C at the growth rate of 1–2 mg/h is from 0.8 to $3 \cdot 10^2$ cm^{-2}. Types Ib and IIb diamond single crystals grown in the thermodynamic stability region at 1280–1450°C at the rate of 3.5–5 mg/h exhibit the dislocations density of 1.1–2.2, which is an order of magnitude higher as compared with the single crystals grown at 1420–1500°C. The dislocations density in diamonds produced by spontaneous recrystallization of graphite in carbon solution at the temperature of 1280–1350°C at the growth rate of 20–25 mg/h is $1.06\text{–}1.35 \cdot 10^6$ cm^{-2}. Increase of the rate of diamond growth results in the considerable increase of the dislocations density.

References

1. M.P.Shaskol'skaya, Articles about Properties of Crystals, Nauka, Moscow (1987) [in Russian].
2. A.Kadich, E.Edelen, Gauge Theory of Dislocations and Disclinations, Springer, Berlin (1983).
3. D.P.Grigor'ev, I.I.Shafranovsky, *Zapiski Vseroc. Min. Obshchestva*, **I**, Issue 1-2,Ch. 70 (1942).
4. A.A.Kukharenko, V.M.Titova, *Scientific Notes of LSU*, **215**, 26 (1957).
5. R.B.Heimann, Auflosung von Kristallen. Theorie und Technische Anwendung, Springer-Verlag, New York (1975).
6. K.Sangwal, Etching of Crystals: Theory, Experiment, and Application, Elsevier Science Publishers B. V., Amsterdam (1987).
7. J.Friedel, Dislocations, Pergamon Press, Oxford-London-Edinburg-New York-Paris-Frankfurt (1964).
8. N.A.Tyapushina, E.K.Naimi, G.M.Zinenkova, Effect of Ultrasound on Crystals with Defects, Izd. Moscow University, Moscow (1999) [in Russian].
9. A.I.Chepurov, I.I.Fedorov, V.M.Sonin et al., *Eur. J. Mineral.*, **11**, 355 (1999).
10. Yu.N.Pal'yanov, A.F.Khokhryakov, Yu.M.Borzdov et al., in: Extend. Abstr. 6 Int. Kimb. Conf., Novosibirsk, Russia (1995), p.415.
11. Yu.N.Pal'yanov, A.F.Khokhryakov, Yu.M.Borzdov et al., in: Proc. 8 Int. Symp. on Water-Rock Interaction (WRI-8), Vladivostok, Russia (1995), p.95.
12. A.Mussi, D.Eyidi, A.A.Shiryaev, *J. Rabier, Phys. Stat. Solidi A*, **210**, 191 (2013).
13. Yu.N.Pal'yanov, A.F.Khokhriakov, Yu.M.Borzdov et al., in: Abst. Joint XV AIRAPT & XXXIII EHPRU Conf. Warsaw, Poland (1995), p.314.
14. V.A.Fedorov, Yu.I.Tyalin, V.A.Tyalina, Dislocation Mechanisms of the Fracture of Twinning Materials, Izd. Machine-building-1, Moscow (2004) [in Russian].
15. Yu.N.Pal'yanov, A.G.Sokol, Yu.M.Borzdovet et al., *Lithos.*, **60**, 145 (2002).
16. Yu.N.Pal'yanov, Yu.M.Borzdov, A.G.Sokol et al., *Dokl. RAN*, **353**, 233 (1997).
17. M.G.Mil'vidskii, V.B.Osvenskii, Structural Defects in Single Crystals of Semiconductors, Metallurgiya, Moscow (1984) [in Russian].
18. R.H.Wentorf, *J. Phys. Chem.*, **75**, 1833 (1971).
19. H.M.Strong, R.H.Wentorf, *Die Naturwissenschaften*, **59**, 1 (1972).
20. J.Hirt, J.Lote, Theory of Dislocations, New York-St.Louis-San Francisco-Toronto-London-Sydney (1969).