EXPERIMENTAL DETERMINATION OF GRAPHITIZATION THRESHOLDS OF A SINGLE CRYSTAL OF HPHT DIAMOND UNDER THE INFLUENCE OF LASER RADIATION

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We determined thresholds for single and multi-pulse graphitization of HPHT single crystal diamond, finding that graphitization has defect-based character. Nitrogen impurities impact samples without external surfaces, while metal impurities, particularly nickel, affect those with external surfaces. Raman spectra analysis shows that nanocrystalline graphite content increases with higher irradiation energy, while lower interaction energy favor carbine, polyene structures and disordered diamond.

Keywords: Synthetic HPHT Diamond; IR/Vis Diamond Absorption Spectra; Defect-Based Graphitization; Graphitization Thresholds; Graphitized Diamond Raman.

ЭКСПЕРИМЕНТАЛЬНОЕ ОПРЕДЕЛЕНИЕ ПОРОГОВ ГРАФИТИЗАЦИИ МОНОКРИСТАЛЛА HPHT-АЛМАЗА ПОД ВОЗДЕЙСТВИЕМ ЛАЗЕРНОГО ИЗЛУЧЕНИЯ

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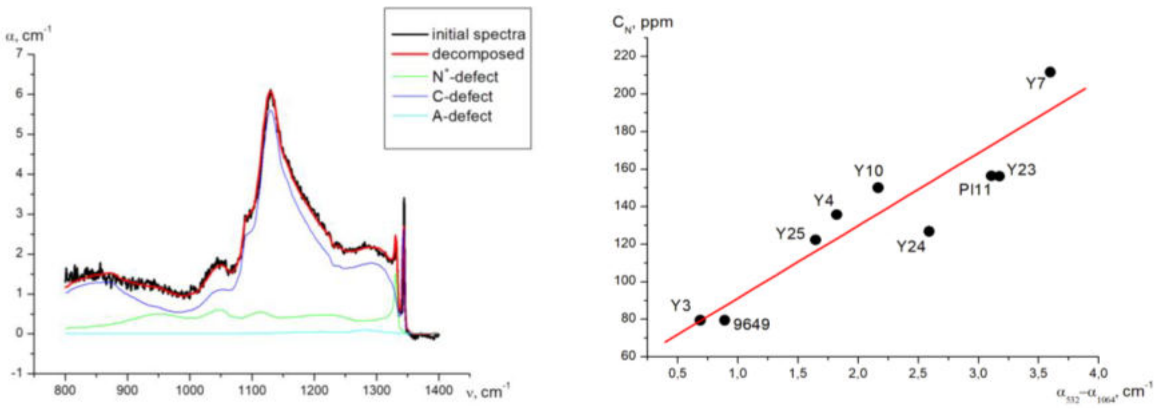
Определены пороги одно- и многоимпульсной графитизации монокристалла HPHT алмаза. Примеси азота влияют на образцы без внешних поверхностей, примеси металлов - на образцы с внешними поверхностями. Анализ спектров КРС показывает, что содержание нанокристаллического графита увеличивается с увеличением энергии облучения, а при взаимодействии с меньшими энергиями образуется большое количество карбина, полиеновых структур и разупорядоченного алмаза.

Ключевые слова: синтетический HPHT-алмаз; ИК-спектры поглощения алмаза; графитизация на дефектах, пороги графитизации; КРС графитизированного алмаза.

Introduction. Laser radiation is highly effective for material modification, enabling micro-profiling of diamond surfaces, creating diamond diffraction optical elements (like Fresnel lenses and beam focusers[1]), forming graphite tracks, and increasing crystal defect concentration. Few studies have focused on the graphitization thresholds of diamond under laser radiation, mostly involving natural diamonds and CVD-grown synthetic films[2, 3]. This study aims to examine the graphitization of synthetic diamond single crystals grown by the HPHT method under pulsed laser radiation.

1. Research material. We used synthetic HPHT type Ib diamond plates with (111) and (100) orientations, grown in the Ni-Fe-C system. The plates measure approximately 2x3 mm and are 0.36 to 1.23 mm thick. Before use, the samples were treated in $K_2Cr_2O_7$ at 80°C for 5 hours, then washed with deionized water in an ultrasonic bath.

2. Research methods. To characterize the samples, we recorded IR and visible absorption spectra. IR absorption spectra in the 800-1400 cm^{-1} region includes several overlapping bands linked to various nitrogen crystal defects (fig. 1a). The diamond plates were processed using Nd^3:YAG laser radiation at wavelengths of 1064 and 532 nm, with a pulse duration of ~20 ns. The average energy density E_s was varied by laser energy and beam focusing. After the irradiation Raman spectra of the diamond surface were taken.



a *b*

Fig. 1. Example of decomposition of the IR spectrum of the Y10 sample(a) and difference in absorption coefficients at 532 and 1064 nm on the nitrogen defects concentration(b)

3. Results and their discussion. The absorption coefficient dependence (fig.1b) could not be directly determined due to imperfect plane parallelism of the samples and the effect of metal impurities on absorption.

According to source [2], which studies CVD type IIa diamonds, the primary graphitization process is multiphoton absorption at the diamond lattice. In our case (fig. 2), graphitization occurs locally, this suggests that graphitization primarily appear in structural defects and/or their segregation areas, with nitrogen and metal impurities playing a significant role in the process. All samples could be divided into 2 groups, with and without external surfaces. These surfaces, formed during the cooling of the reaction zone under highly nonequilibrium conditions, contain more impurities (mainly metal-solvents) than the crystal's interior.

Table 1

Results of research on graphitization of synthetic diamond

Sample	Y7	Pl20	Y25	Y26	9649	Y24	Pl11	Y10	Y23	Pl13
E_s, J/cm^2	7,6	9,3	8,0	8,0	6,4	6,8	14,1	2,6	2,6	2,0
Orientation	111	100	100	111	111	111	100	111	111	100
λ, nm	1064	1064	532	532	532	532	532	1064	1064	532
Pulses	1							32	20	1300
C_N, ppm	156,1	-	122,2	-	79,4	126,7	156,3	150	211,6	280,9

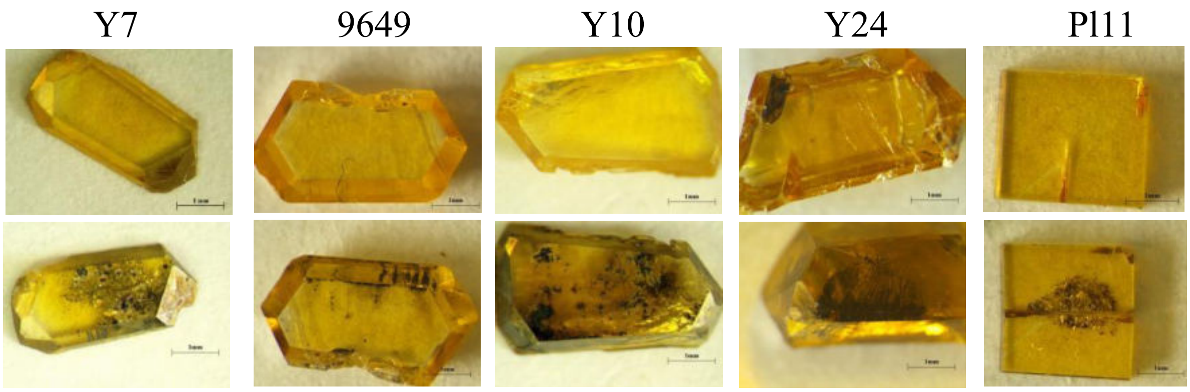


Fig 2. Photos of samples before graphitization (top) and after (bottom)

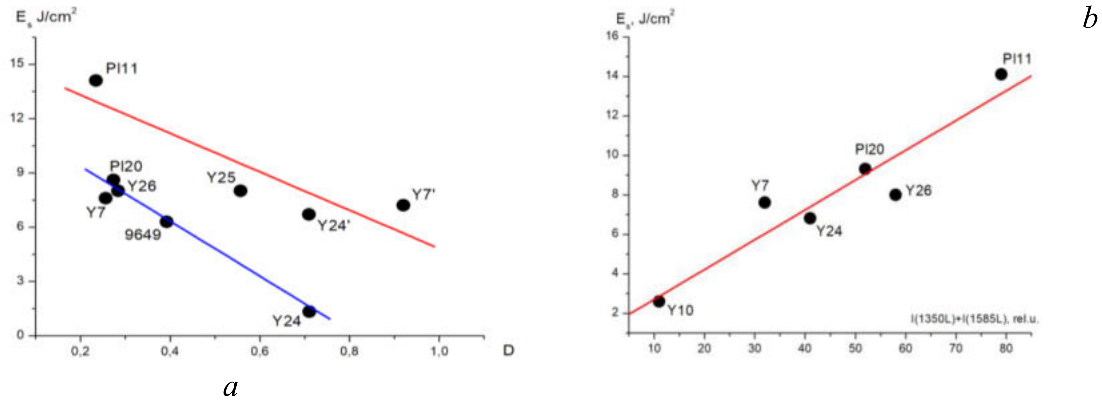


Fig.3 E_s on the optical density for samples with(blue line) and without (red line) external surfaces (a), E_s on the total content of nanocrystalline graphite (b)

Figure 3a reveal a clear distinction between samples with and without external surface. Given that absorption is almost entirely due to impurities, the multiphoton absorption model described in [2] is invalid, as indicated by the weak dependence of graphitization thresholds on the radiation wavelength.

Table 2

Raman spectra decomposition results

Position	Carbon type	Line intensity, rel. units					
		Y24	Y10	Y26	Y7	Pl11	Pl20
430 cm^{-1}	Disordered diamond	20	40	0	3	2	10
710 cm^{-1}		8	10	2	5	2	3
1180 cm^{-1}	Disordered graphite	70	60	50	88	55	60
1350L cm^{-1}	Nanocrystalline graphite	20	8	18	22	42	5
1350 cm^{-1}	Amorphous carbon	130	130	80	109	95	170
1420 cm^{-1}	Polyenes	5	10	2	9	0	0
1530 cm^{-1}	Amorphous carbon	180	185	120	200	118	123
1585L cm^{-1}	Nanocrystalline graphite	21	3	40	10	37	47
2085 cm^{-1}	Carbine	15	24	1	3	2	0

Note. L - approximation by the Lorentz function, otherwise - by the Gaussian function

The Raman spectra analysis (table 2) revealed a diverse surface composition post-irradiation, comprising nanocrystalline graphite, amorphous carbon, disordered diamond, graphite, polyene structures and carbine. Nanocrystalline graphite content increases with increasing the irradiation energy (fig. 3b), while lower irradiation energy (E_s < 7J/cm^2) favor carbine, polyene and disordered diamond.

Conclusion. Analysis of the IR and visible absorption spectra showed that the absorption coefficient depends on the impurity composition of the samples (fig. 1b). The thresholds for single-pulse and multi-pulse graphitization of synthetic HPHT diamond single crystals were experimentally estimated (table 1). Graphitization occurs locally, with nitrogen impurities playing a significant role in samples without external surfaces, and metal impurities in samples with external surfaces (fig. 3a). The Raman spectra analysis shows that nanocrystalline graphite increases with higher irradiation energy (fig. 3b), while lower interaction energy (E_s < 7J/cm^2) favor carbine, polyenes and disordered diamond.

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