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Laser-induced breakdown spectroscopy as an effective method for the identification of diamonds

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Abstract. **We investigate the possibility of using the method of laser-induced breakdown spectroscopy to identify diamonds and detect changes in atomic bonds in crystals due to the presence of impurities or due to changes in the hybridisation state of carbon atoms. It is found that laser-induced graphitisation of the diamond surface leads to a significant increase in the sensitivity of the method.**

Keywords: *laser-induced breakdown spectroscopy, laser ablation, diamonds, graphitisation.*

It is known that the absolute majority (up to 98%) of natural diamonds bear an admixture of nitrogen with a concentration of tens to hundreds of ppm, and such diamonds have yellow or yellowish green colour. On the other hand, modern technologies, in particular using the high pressure – high temperature (HPHT) method, make it possible to grow large single crystal diamonds, including those doped with various impurities, both for jewellery industry and for scientific and technological applications [1]. The structure of synthetic diamonds also contains an admixture of nitrogen, but in significantly lower (to units of ppm or less) concentrations. Structural and, as a result, spectral properties of natural and synthetic diamonds can in turn be changed as a result of additional thermal or radiation effects; therefore, the detection of such changes by various spectral methods is an important task [2].

Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy that is constantly finding new applications and is highly demanded. The advantages of LIBS are determined by the possibility of simultaneous multi-element qualitative or quantitative analysis, including rapid analysis of the chemical composition of a substance in any aggregate state, and are complemented by the capabilities of remote analysis. Modern technologies allow the development of portable and mobile compact laser systems and LIBS measurements at distances from few to several tens of meters [3].

It was previously shown that the LIBS method makes it possible to identify with a high probability both the geographical origin of natural diamonds and the laboratory at which synthetic diamonds were grown [4]. The analysis of the spectra of the laser-induced plasma of the samples was carried out not by the atomic emission lines of the elements, but by the molecular emission bands of C_2 and CN. The basis for this approach was the results of studies on the identification of organic compounds by the LIBS method, when it was found that small changes in the intensities of the molecular bands of C_2 and CN are also determined by the difference in the structures of atomic bonds in matter [5].

Laser-induced graphitisation of polycrystalline diamond plates grown by the CVD method and their ablation regimes as functions of pulsed laser radiation parameters were studied by Kononenko et al. [6], who found that graphitisation occurred jumpwise in time and showed that in the performed experiments a layer of nanocrystalline graphite was formed during a single laser pulse.

In this paper, we present the results of studies using the LIBS method of laser ablation and identification of synthetic diamonds using C_2 and CN molecular bands in the presence of laser-induced graphitisation of the surface of the samples in question.

Multisectoral plates of yellow synthetic single crystal diamonds with a transverse size of 5 × 5 mm and a thickness of 1 mm, grown at New Diamond Technology LLC (Russia) by the HPHT method, were investigated. The nitrogen concentration in the samples ranged from a few to several tens of ppm. An LQ-129 pulsed Nd^{3+}:YAG laser (Solar LS, Belarus) operating at a wavelength of 1064 nm with a pulse repetition rate of 2 Hz, a pulse duration and energy of 17 ns and 230 mJ was used as a radiation source during LIBS. The energy density of the laser beam on the target surface was about 1 kJ cm^{-2}. The plasma spectra of diamonds were recorded in an argon atmosphere (chemical interaction of plasma with air was excluded) with an AvaSpec-ULS2048L-USB2 spectrometer (Avantes, the Netherlands). The scheme of the experimental setup for carrying out LIBS measurements is identical to that used previously in the analysis of nanocarbon films [7]. The triggering of the laser, the synchronisation of its operation with the spectrometer, the registration and processing of plasma spectra were carried out using our own software [8]. The mathematical processing of each plasma spectrum relied on a key procedure, i.e., the normalisation procedure, which is an important part of modern spectral processing algorithms in the LIBS method and consists in calculating the relative contribution of the analysed emission band to the total plasma emission spectrum [8]. The Raman spectra of the original and irradiated diamond plates were measured using an inVia confocal Raman microscope (Renishaw, the United Kingdom) equipped with a He – Ne laser.

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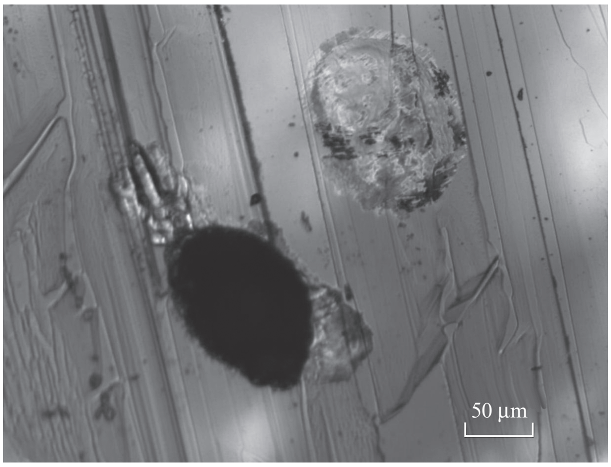

Figure 1. Photograph of diamond surface spots after laser irradiation (before and after graphitisation).

Different sectors of the studied samples were exposed to laser pulses (from one to 30 at one point). It is obvious that the effect of the first laser pulses on the surface is determined by their interaction with structural surface defects. For subsequent pulses, the interaction with the sample surface already begins to be determined by the absorption of a robust graphite-like film that is formed on the diamond surface (Fig. 1).

For the sectors of the non-irradiated diamond plate with (100) and (111) crystallographic orientations, the differences in the structures of atomic bonds are clearly manifested in the Raman spectra. In the spectrum of the sector with the (111) orientation, in addition to the D band (1332 cm^{-1}), characteristic of bulk diamond crystals, additional bands appear, which indicate the presence of a more disordered diamond structure due to the formation of a significantly larger number of various bonds between carbon atoms. The spectra of the surface modified as a result of laser-induced graphitisation are characterised by a sharp broadening of the D band and the appearance of the G band (1600 cm^{-1}) characteristic of the sp^2 hybridisation of carbon atoms (C = C bonds) (Fig. 2).

In the experiments performed, a rapid graphitisation of the surface of the studied diamond plate was observed after 10–12 laser pulses. From the full emission spectrum of the plasma of diamond samples (the characteristic spectrum of a nanodiamond film is given in [7]), the most intense bands were selected that belong to C_2 and CN in the spectral ranges from 495 to 517 nm and from 378 to 389 nm, respectively. An analysis of the intensities of the C_2 and CN emission bands in LIBS spectra showed the presence of two stationary ablation regimes of the sample; the transient process lasted for about five laser pulses (Fig. 3). A significant increase in the number of C = C double bonds characteristic of a graphitised sample surface led to a sharp, up to five times, increase in the emission intensity of the C_2 band, but the increase in the emission intensity of the CN band turned out to be less significant.

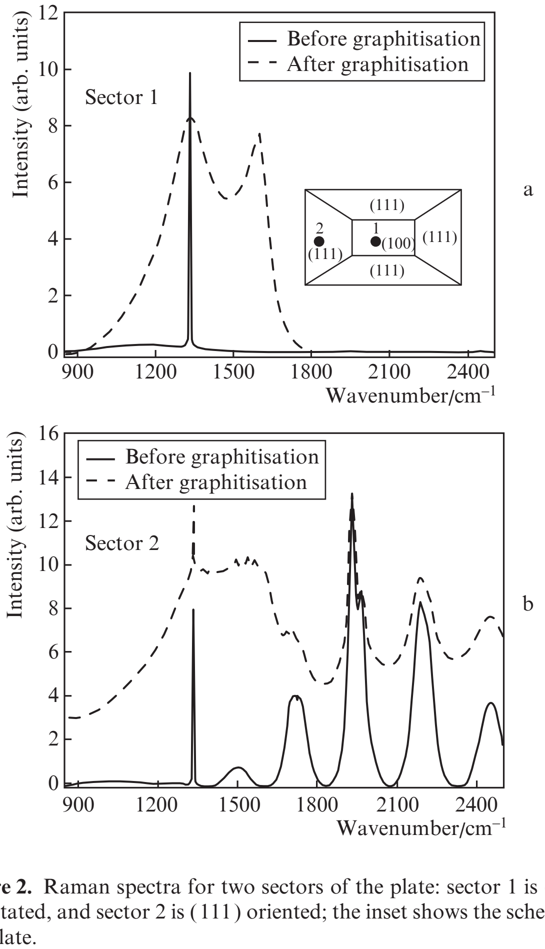

Figure 2. Raman spectra for two sectors of the plate: sector 1 is (100) orientated, and sector 2 is (111) oriented; the inset shows the scheme of the plate.

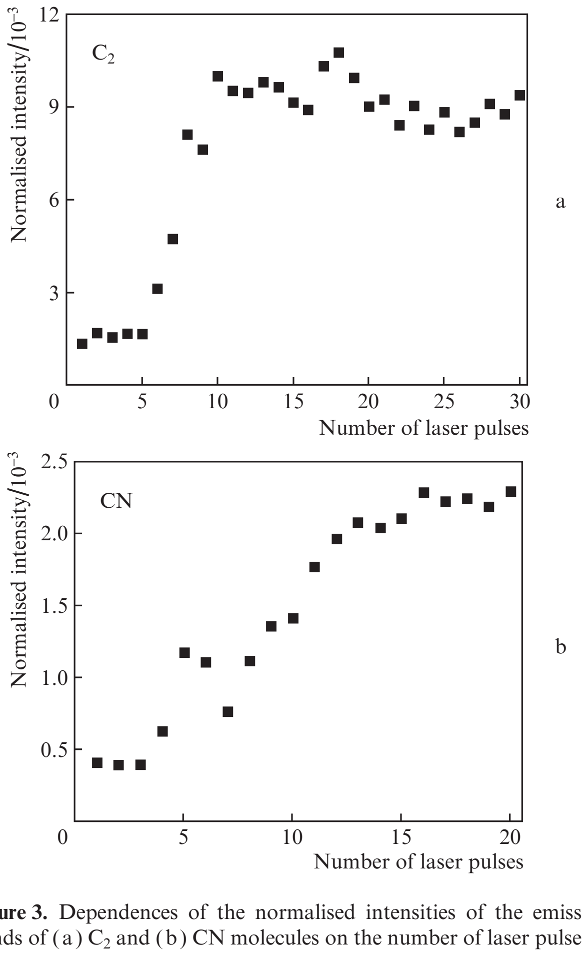

Figure 3. Dependences of the normalised intensities of the emission bands of (a) C_2 and (b) CN molecules on the number of laser pulses.

The spectra obtained in each laser pulse and normalised to its maximum value for each of the stationary ablation regimes were combined in a series (Fig. 3), from which the average spectra were calculated under the assumption of a normal intensity distribution [8]. These values for the emission bands of CN and C_2 in the plasma obtained during ablation of the graphitised diamond surface for two plate sectors (points 1 and 2, inset in Fig. 2a) are presented in Fig. 4. Obviously, in this case, changes in the intensities of the C_2 and CN emission bands are determined by differences in the bond structure of carbon atoms and in the concentration of nitrogen atoms, and similar changes were observed for all the samples in question. Thus, the possibility of using the LIBS method to identify structural differences in atomic bonds, in particular when carbon hybridisation changes in different carbon materials, in order to detect other bonds (for example, CN) in comparative experiments for a series of samples, is unambiguously confirmed. The assumption about such possibilities of the method was expressed previously and was a consequence of the analysis of changes in the band intensities in the LIBS spectra of nanocarbon films with different bond structures of carbon atoms [7].

It should also be noted that the methods of absorption IR Fourier transform spectroscopy have been previously used to study multisectoral diamond plates, similar to those considered in the present work, but already doped with boron [9]. It turned out that, like our data on the ratio of nitrogen concentration levels in the sectors of the crystal with the (111) and (100) orientations (Fig. 4), the boron concentration in the sector of the crystal with the (111) orientation is significantly higher than that in the sector with the (100) orientation, which confirms the large disorder of the crystal structure in the first case.

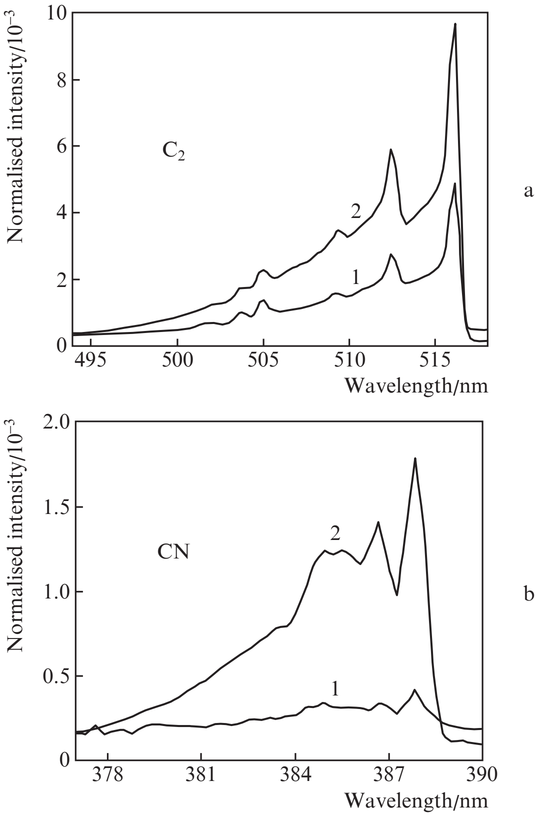

Figure 4. Intensities of the emission bands of (a) C_2 and (b) CN for sectors 1 and 2 with (100) and (111) orientations, respectively (points 1 and 2, see the inset in Fig. 2a).

Thus, we have shown that laser-induced graphitisation of diamond, accompanied by the establishment of a steady-state ablation regime, is a process that contributes to a significant increase in the sensitivity of the LIBS method. The presence of a stationary ablation regime should lead to a more accurate quantitative analysis of diamond samples by this method. Analysis of a series of plates of nitrogen-containing diamonds with a nitrogen concentration of several ppm showed the possibility of identifying synthetic diamonds due to changes in the structural bonds of carbon atoms and the level of nitrogen doping both within one multisectoral plate and in the case of a series of plates with different degrees of doping. Due to the possible influence of the selectivity of the evaporation of elements, further studies of the sensitivity of the LIBS method are needed for other dopants under conditions of graphitisation of the diamond surface.

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