

# Peculiarities of the pulsed photoresponse from a 2-A diamond to UV laser radiation at 308 nm

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Results of studies of the photoresponse of a 2-A type diamond to a pulsed laser radiation at 308 nm are reported. An anomalous increase in the amplitude and duration of the photocurrent at high energy density of laser radiation has been revealed. It was found that an additional component of the pulse photocurrent appears at the energy density of 0.7–1 J/cm<sup>2</sup> being independent of the duration and intensity of laser pulses. It is proposed to use this effect to increase the current in diamond optoelectronics switches controlled by a spontaneous UV radiation.

## Introduction

Diamond has a number of unique properties, which provide for its practical use not only in jewelry. Thus, diamond has the highest hardness among the known natural materials.<sup>1</sup> This makes it a perfect material for production of cutters.<sup>2</sup> It is known, for example, that already ancient Romans used diamond plates to cut sapphires.<sup>2,3</sup>

Another one outstanding property of diamond – its high thermal conductivity – has also been known since ancient time.<sup>2</sup> At room temperatures the thermal conductivity of diamond is as high as 20 W/(cm · K), which is several times higher than the thermal conductivity of copper [no higher than 4–5 W/(cm · K)] [Refs. 1, 4]. Therefore, diamond is also used for heat sink production.<sup>5</sup>

Since the middle of the twentieth century, the high radiation hardness and tissue-equivalence (atomic number of diamond is 6, which is close to the mean atomic number of biological tissues ~ 7.5) of diamond has provided its use in detection of nuclear radiation and dosimetry.<sup>2,5,6</sup>

Besides, diamond is intended for use in microelectronics devices to be operated under adverse conditions: intense radiation, high temperature, and chemically hostile environments.<sup>2,3,5,7,8</sup> Thus, for silicon devices the limiting operation temperature does not exceed 300–350°C, while for diamond devices the operation temperature can be as high as 1000°C.

The wide band gap of 5.5 eV provides for high radiation tolerance and transparency of pure diamond up to the energies of deep UV. Therefore, diamond finds expanding use as a material for optoelectronics, in the first turn, in solar-blind UV detectors.<sup>9–12</sup> These detectors are characterized by high sensitivity to UV radiation, but far lower one to the visible radiation. Diamond is also suitable for X-ray measurements.<sup>13,14</sup>

Another one promising field is the development of UV-controlled high-voltage diamond switches of high powers.<sup>15–17</sup> In this case high breakdown voltage

> 1 MV/cm increases the operating voltage of a switch, the high resistivity > 10<sup>12</sup> Ω · cm provides for low leakage current, and the highest thermal conductivity ensures efficient heat dissipation. Besides, the diamond permittivity of 5.68 [Ref. 1], which is relatively low as compared to that of other semiconductors, determines the ultrashort turn-on time (tens of femtoseconds in the theoretical limit),<sup>16</sup> and short lifetime of charge carriers in natural diamonds (100–400 ps) causes the turn-off time comparable with that in gallium arsenide switches, in which the charge carrier lifetime is ~ 100 ps [Ref. 2]. Moreover, CVD (chemical vapor deposited) diamonds, the technology of whose synthesis is rapidly developing in recent time,<sup>18</sup> have much shorter charge carrier lifetime than that of natural diamonds.<sup>19</sup>

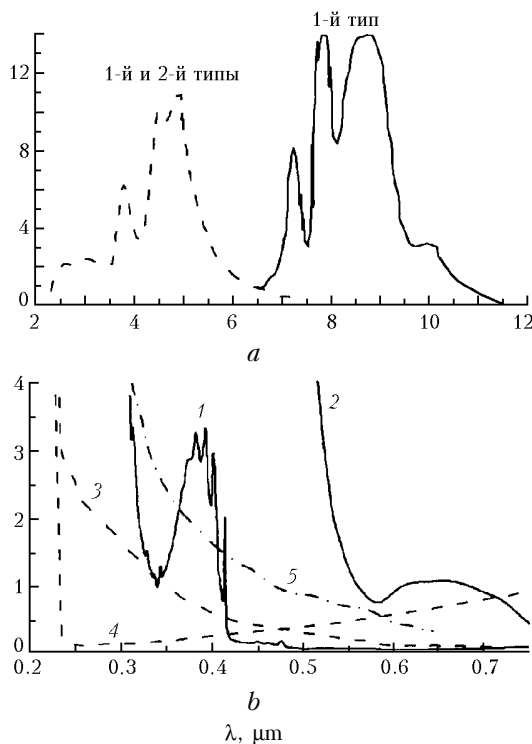
The optoelectronics devices described, as well as detectors of nuclear radiation, employ the property of semiconductors to reduce their resistance under exposure to radiation (no matter what is its nature: electromagnetic or corpuscular) capable of generating free charge carriers. In the case of diamond, this reduction can achieve 15 orders of magnitude. This phenomenon is known as photoresponse.

This paper presents the results of investigation into the phenomenon of pulsed photoresponse in a 2-A diamond under the action of a laser UV irradiation at 308 nm. The anomalous increase in the amplitude and duration of the photocurrent passing through diamond has been discovered for the first time at high energy density of the 308-nm incident radiation. The threshold energy density in this case is independent of (or weakly dependent on) the duration of the excitation pulse.

## 1. Brief classification of diamonds

All natural diamonds contain a natural nitrogen impurity, which is also called the technological one. Nitrogen at a lattice point of the diamond creates a deep donor level ~ 1.7 eV, which cannot be thermally

activated, in the band gap. The concentration of nitrogen impurity largely determines the optical and electrical properties of diamonds. Historically, diamonds were classified into two types based on their IR absorption spectra.<sup>20</sup> As can be seen from Fig. 1*a*, all diamonds have a wide absorption band from 2 to 6  $\mu\text{m}$ , which is assigned to absorption by the diamond lattice. The wide 8  $\mu\text{m}$  band is associated with the nitrogen impurity. Therefore, diamonds showing measurable absorption in the region  $> 8 \mu\text{m}$  and having the concentration of the nitrogen impurity up to  $10^{21} \text{ cm}^{-3}$  were classified to the first type, while diamonds showing no absorption in this region were classified to the second type and referred to as nitrogen-free for a long time. Actually, such diamonds include nitrogen at the concentration up to  $5 \cdot 10^{18} \text{ cm}^{-3}$  [Ref. 2].



**Fig. 1.** Absorption spectra of natural diamonds in the IR (*a*) and UV and visible (*b*) regions; source from Ref. 2 (*a*), source from Ref. 21 (*b*; curves 1, 3, 4), and source from Ref. 22 (*b*; curves 2, 5).

According to the international classification, diamonds of the first type are subdivided into 1-A and 1-B diamonds. Diamonds of the 1-A type make up  $\sim 98\%$  of all natural diamonds (Fig. 1*b*, curve 1). Nitrogen in them forms predominantly volume defects (two- and many-atom formations, segregates, etc.), which cause deep donor levels from 1.7 to 4.1 eV below the bottom of the conduction band.<sup>2</sup> The diamond of 1-B type incorporates most rare natural diamonds ( $\sim 0.1\%$  of all diamonds), in which nitrogen creates predominantly point defects in the form of substitutional atoms, which imparts the yellow color to such crystals (Fig. 1*b*, curve 2). At the same time, most synthetic diamonds grown under high pressure

and temperature are diamonds of the 1-B type. The resistivity of the first-type diamonds achieves  $10^{16} \Omega \cdot \text{cm}$ . In the Russian classification of diamonds, the 1-A type is subdivided according to the types of defects formed by nitrogen, which lead to differences in absorption spectra (see Ref. 2).

Due to the lower nitrogen concentration, diamonds of the second type demonstrate a robust edge of the fundamental absorption starting from  $\sim 226 \text{ nm}$ , which corresponds to the band gap width of the ideal diamond (Fig. 1*b*, curves 3 and 4).

It was found, in turn, that some of the second-type diamonds include a boron impurity in the form of substitutional atoms with the concentration up to  $5 \cdot 10^{16} \text{ cm}^{-3}$  and have a blue tint. These diamonds are classified to the 2-B type (Fig. 1*b*, curve 4). The boron impurity creates the acceptor level with the activation energy  $\sim 0.36 \text{ eV}$  in the band gap; therefore, at room temperatures this level is activated only partly. Nevertheless, a 2-B diamond is a *p*-type semiconductor and has the resistivity of  $10\text{--}10^3 \Omega \cdot \text{cm}$  [Ref. 2]. The 2-B diamonds have the lowest nitrogen concentration among all natural diamonds, namely,  $\sim 10^{15} \text{ cm}^{-3}$ . In Russian deposits the 2-B diamonds have not been found.<sup>2</sup>

The content of other impurities found in natural diamonds is too low to significantly affect their optical and electrical properties. In addition to the impurities, diamonds have various intrinsic defects: vacancies, interstitial atoms, dislocations, and others. All these defects create a certain relief of the density of states in the band gap, which manifests itself in the optical and electrical properties of diamonds. In particular, natural diamonds underwent to plastic deformations may have the color from pink to brown (Fig. 1*b*, curve 5).

Thus, 2-A diamonds (Fig. 1*b*, curve 3) are low-nitrogen crystals with the resistivity higher than  $10^{13} \Omega \cdot \text{cm}$ . The low content of nitrogen provides for high mobility of charge carriers (up to  $2500 \text{ cm}^2/(\text{V} \cdot \text{s})$  for electrons and up to  $2100 \text{ cm}^2/(\text{V} \cdot \text{s})$  for holes), as well as repeatability of optical and electrical properties. It is mostly for this reason that 2-A diamonds are most widely used in various optoelectronic devices. Besides, the use of diamonds as detectors of nuclear radiation has shown that high concentration of the nitrogen impurity deteriorates the counting properties of such detectors due to the effects associated with volume charge accumulation.<sup>23</sup> In the study of pulsed photoresponse, the 2-A diamonds have demonstrated the photoresponse amplitude about tenfold higher than that in diamonds of other types.<sup>24</sup> It is also important that 2-A diamonds are of little use in jewelry.

Thus, optoelectronic applications utilize mostly 2-A natural diamonds. In recent time the synthesis of CVD diamonds has been actively developed. In the properties and quality, CVD diamonds are close to 2-A natural diamonds, but the polycrystal structure of the CVD diamonds and their high defectiveness are constraints in this field.

## 2. Experimental equipment and measurement technique

To study the pulsed photoresponse of diamonds, we used three laser systems designed at the Institute of High-Current Electronics SB RAS, which emitted laser pulses of different duration at the wavelength of 308 nm. The parameters of these lasers are summarized in the Table.

Parameters of the laser systems

Laser	Mixture	Wavelength, nm	Pulse duration at half-maximum, ns	Pulse energy, J	Ref.
Foton-2	HCl:Xe:Ne = 1:10:750	308	20	up to 0.35	25
LIDA T	HCl:Xe:Ne = 1:6:560	308	50	up to 1	26
LIDA D	HCl:Xe:Ne = 1:8:1510	308	120	up to 0.8	27

The laser radiation was incident onto a diamond radiation detector (DRD) made at Alameda Applied Sciences Corporation. The DRD is based on a  $3 \times 1 \times 0.5$  mm 2-A diamond crystal placed in a coaxial holder with the wave resistance of  $50 \Omega$  (Ref. 17). The electric contacts to the diamond were made by deposition of the Ti/Pt/Au three-layer structure onto the opposing  $3 \times 0.5$  mm faces of the crystal. The  $3 \times 1$  mm face was exposed to laser radiation.

One of the DRD contacts was connected to a capacitor charged from a dc voltage source (Fig. 2). At the pulsed decrease in the resistance of the diamond crystal, the capacitor discharged through a load.

The design of the electric circuit provided for the load resistance of  $25 \Omega$ . Earlier<sup>28</sup> we used the electric circuit with a  $50\text{-}\Omega$  load, which caused lower DRD currents. All the experimental data presented below were obtained with the capacitor charging voltage of 250 V, which provided for the strength of the electric field applied to the crystal equal to  $2.5 \text{ kV/cm}$ . Alternation of the voltage sign led only to alternation of the sign of the recorded signal, rather than to the change in the character of the obtained dependences, which is indicative of a good symmetry of the system.

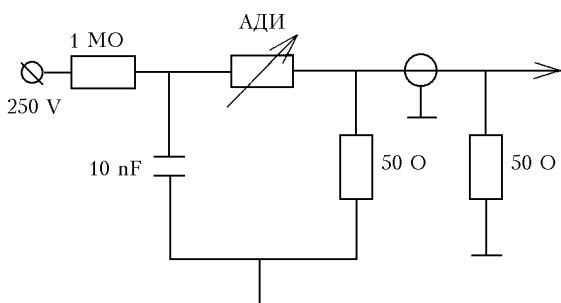


Fig. 2. Electric circuit for measurement of pulsed photoresponse of diamond.

The pulsed voltage across the load was measured with a TDS-220 or TDS-224 digital oscilloscope (TEKTRONIX Inc.). The laser pulse energy was measured with an IMO-2N calorimeter or a PE25-SH pyroelectric detector (OPHIR OPTRONICS Ltd.). The laser pulse shape was recorded with a FEK-22 vacuum photodiode. The measurement technique has been described in detail elsewhere.<sup>28</sup>

## 3. Experimental results and discussion

As we have reported earlier, as a diamond is exposed to the laser radiation [no matter whether it falls within the diamond absorption band ( $\lambda < 226 \text{ nm}$ ) or the absorption is caused by an impurity or lattice defects ( $\lambda > 226 \text{ nm}$ )], DRD follows to indicate the pulse shape in the nanosecond range (see Fig. 4 in Ref. 28). However, as the amplitude of the switching signal approaches the charging voltage of the switched capacitor, the DRD signal experiences distortions, but this is the effect of the electric circuit rather than a diamond property.<sup>29</sup>

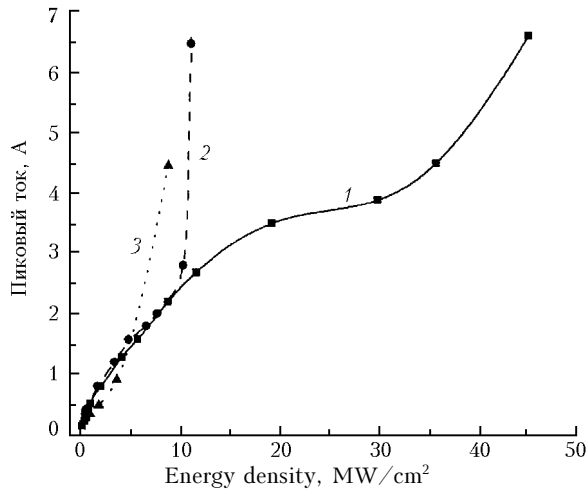
The peak-point current (see Fig. 5 in Ref. 28) under these conditions is limited by the load resistance, which causes saturation of the current as a function of the intensity. The higher the absorption coefficient for the incident radiation, the more rapidly the saturation occurs. Correspondingly, the measured sensitivity decreases (see Fig. 6 in Ref. 28). As the radiation wavelength decreased, the sensitivity increased because of the growing absorption coefficient.

Thus, to obtain the maximum current through the diamond, it is necessary to use radiation that is fairly well absorbed. However, in this case the radiation is absorbed in a thin layer. For radiation at 222-nm wavelength the virtually complete absorption occurs in the layer  $\sim 30\text{--}50 \mu\text{m}$ , that is, only  $1/10$  part of the crystal takes part in the process under these conditions. In such a case, in spite of the high thermal conductivity of diamond, graphitizing of the surface layer is possible in the case of switching of high powers. Therefore, a reasonable question arises: whether or not is it possible to achieve the currents with the amplitude as that at irradiation with 222-nm light in the case of diamond excitation by the radiation providing for the volume absorption (for example, at 308 nm)? It could be a natural move to increase the peak intensity of radiation.

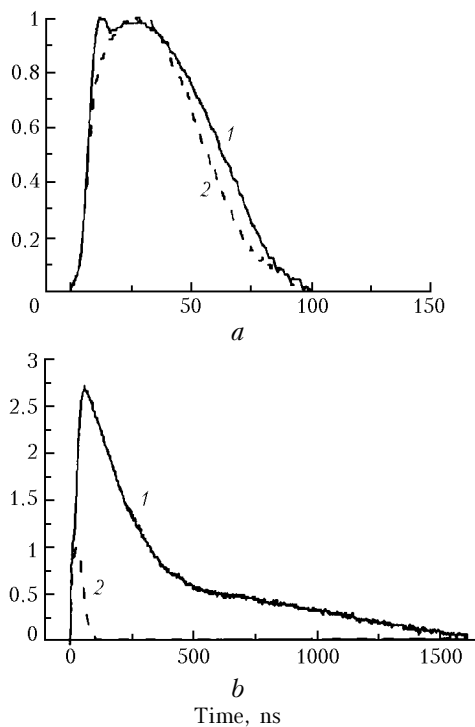
The experiments have shown that as the intensity of radiation with the wavelength of 308 nm and the full duration at half-maximum of 20 ns has increased up to  $\sim 35 \text{ MW/cm}^2$ , the amplitude of the DRD current sharply increased (Fig. 3).

By varying the pulse duration, we have found that as it increased, this effect was observed at lower peak intensities. If the duration is equal to 50 ns, then this effect appears already at the intensity  $\sim 10 \text{ MW/cm}^2$ , but if it is 120 ns, the effect is observed at the intensity  $\sim 5 \text{ MW/cm}^2$ . The increase of the current under these conditions led also to elongation of the DRD pulse (Fig. 4), that is, in the normal mode the DRD pulse

practically copied the laser pulse shape (Fig. 4*a*), but in the anomalous mode, when the current increased sharply, the pulse duration achieved 1  $\mu\text{s}$  and longer (Fig. 4*b*).



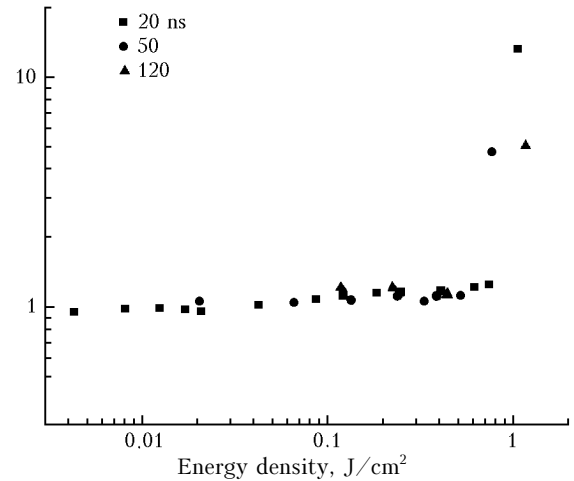
**Fig. 3.** Peak DRD current as a function of the intensity of 308-nm laser radiation at different pulse duration at half-maximum: 20 (curve 1), 50 (2), and 120 ns (3).



**Fig. 4.** Laser (curve 2) and DRD (curve 1) pulses in the normal (*a*) and anomalous (*b*) modes.

Having drawn the dependence of the DRD pulse duration on the incident energy density (Fig. 5), we found that this effect appeared at roughly the same laser radiation energy density of 0.7–1  $\text{J}/\text{cm}^2$  for any pulse duration. If the diamond absorption coefficient at 308 nm is taken to be 1.5  $\text{cm}^{-1}$  [Ref. 22] and the refractive index is assumed to be 2.53 [Ref. 1], then the absorbed energy for the 0.5-mm thick crystal is

7% of the incident energy. Then the increase of the current amplitude and the DRD pulse duration occurred under our conditions at the absorbed laser radiation energy  $\sim 1\text{--}1.4 \text{ J}/\text{cm}^3$ .



**Fig. 5.** Relative duration at half-maximum of the DRD pulse as a function of the energy density for different duration of the laser pulse.

This effect has already been reported in the first papers on 2-A diamond switching by the laser radiation, but at the wavelengths less than 250 nm. Gliniski et al.,<sup>30</sup> studied the pulsed photoresponse in 2-A diamond at the wavelength of 222 nm and the pulse duration at half-maximum  $\sim 7$  ns. At the strength of the field applied to a sample higher than 6  $\text{kV}/\text{cm}$  and partial irradiation of the diamond crystal (irradiation of the 1/3 interelectrode gap near the cathode), the duration at half-maximum of the current pulse through the diamond increased up to 60 ns. As this took place, gradual decrease of the intensity from 0.5 to 0.2  $\text{MW}/\text{cm}^2$  caused the splitting of the photoresponse signal into two components and to the increase of the gap between these components up to 40 ns. For the 50  $\Omega$  load and the radiation intensity of 0.32  $\text{MW}/\text{cm}^2$ , the amplitude of the current across the diamond achieved  $\sim 0.1$  A for the normal component and  $\sim 0.25$  A for the additional component. It is characteristic that irradiation of the entire interelectrode gap or partial irradiation near the anode did not lead to appearance of the anomalous component of the current pulse. Based on this circumstance, the observed effect was associated in Ref. 30 with the injection of electrons from the cathode because of accumulation of trapped holes near it. For this to take place, a certain strength of the external field must be provided.

Later on, the same research team published<sup>31</sup> similar results for the laser excitation of a 2-A diamond at the wavelength of 193 nm and the pulse duration at half-maximum of 10 ns. However, in that case, neither splitting nor significant retardation of the current signal was observed, but at the field strength higher than 1.7  $\text{kV}/\text{cm}$  and the intensity ranging from 0.1 to 3  $\text{MW}/\text{cm}^2$  a second peak appeared in the

trailing edge of the pulse. The maximum current up to 4 A was obtained at the field strength higher than 16 kV/cm.

Appearance of this effect on oscillograms was also assigned to injection at contacts. The possible influence of surface state on the appearance of injection was also noted in Ref. 31, because at 193 and 222 nm the radiation is absorbed in a thin layer with the thickness from few to tens micrometers, and in Ref. 15 the described effect was not observed for the wavelength of 355 nm (volume absorption), pulse duration of 30 ps, and the intensity up to 330 MW/cm<sup>2</sup>. However, the results of our study suggest that at the pulse duration of 30 ps this effect could be observed at significantly higher intensities.

In Ref. 32 the appearance of the anomalous component of photocurrent in the 2-A diamond was observed at the wavelength of 248 nm for the radiation intensity higher than 0.05 MW/cm<sup>2</sup>. The field strength in that case was higher than 400 kV/cm. Besides, for this effect to appear, exposure to the visible radiation was needed. In the case at hand, the amplitude of the anomalous component of the photocurrent did not exceed that of the normal component. Based on the need of visible irradiation, Feng et al.,<sup>32</sup> suggested that optically active center in the diamond affect the appearance of the additional photocurrent component.

A somewhat different interpretation of the pulse retardation and current amplification was proposed in Ref. 2, where the effect described in Refs. 30–32 was associated with the appearance of optoelectronic instability in the diamond, i.e., the spectrum of levels in the band gap rearranges under the effect of the external electric field. As a result, the diamond switches into the highly conductive state.

In our opinion, the injection character of this effect is more probable than the manifestation of optoelectronic instability. However, discussion of this issue is beyond the scope of this paper.

It should also be noted that in Ref. 31 this effect was classified as parasitic and some recommendations on how to avoid it were given. Certainly, if the diamond is used as a photodetector, then this effect is unwanted, since the DRD pulse is distorted with respect to the optical pulse. But this effect can find a practical use.

As was noted in Ref. 5, this effect may serve an additional mechanism for increasing the current in laser-controlled diamond optoelectronic switches. However, creation of solid-state diamond switches highly competitive with plasma ones requires their compactness and acceptable cost. Development of the technology of synthesis of CVD diamonds provides for commercial availability of the diamond material; therefore, the use of non-laser UV sources in diamond switches becomes quite urgent. The application of a source of spontaneous UV radiation will not only reduce the cost, but also will provide for compactness of the detector. The sources of spontaneous UV radiation, such as pulsed xenon lamps, excimer and exciplex lamps (excilamps) are characterized by microsecond and longer pulse durations, therefore, the effect of

anomalous increase in the amplitude of the current across a diamond can be used, and a significant increase in the photocurrent duration can be absent in this case. Certainly, it is still unclear whether this effect will manifest itself at the microsecond excitation.

## Conclusion

Thus, at the wavelength of 308 nm and high energy density of 0.7–1 J/cm<sup>2</sup> we have observed an anomalous increase in the amplitude and duration of the pulsed photoresponse current in a 2-A diamond. It has been established that the threshold energy density was almost independent of the pulse duration. The additional component of the pulsed photocurrent appeared in the 2-A diamond at absorption of a portion of the UV radiation (~1–1.4 J/cm<sup>3</sup> under our conditions), and the threshold radiation intensity in this case was inversely proportional to the pulse duration.

Achieving a more thorough understanding of the mechanisms of appearance of the described effect in the diamond and its possible applications requires further experiments to be conducted. In particular, it is necessary to study different crystals with different geometry. The effect of the spectral characteristics of the exciting radiation on the appearance of the anomalous increase of current seems to be interesting as well. Besides, a simple and compact source of spontaneous UV radiation providing for the peak intensity of a few MW/cm<sup>2</sup> at the microsecond pulse duration is needed. We plan to carry out the further studies in these fields.

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