The properties of photoconductivity of the IIa-type diamond related to the band gap structure

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Abstract. We investigate the properties of the photosensitivity spectra of the UV photodetectors based on natural diamond. The effect of the structural defects associated with nitrogen impurities to the photosensitivity is analyzed. We confirm that the polychrome light bias application enhances the photosensitivity of these detectors in the spectral range 240–340 nm due to the quasi-two-photon absorption which originates due to the complicated structure of the band gap impurity states of a natural diamond. The possibility to influence the photosensitivity spectra in the \(\lambda<220\) nm spectral range of these detectors by the polychrome light bias application is revealed.

1. Introduction

Research and development of UV photodetectors and photosensitive materials plays an important role in the growing importance of UV photometry and spectroscopy for a lot of applications in ecology, medicine and others. The important photosensitive material for these applications is the diamond due to the unique semiconducting and physical properties \cite{1, 2}. However the feature of a diamond is high concentration of structural defects associated with nitrogen. These defects have high density of band gap states (\(N_g \leq 10^{18} \text{ cm}^{-3}\)) \cite{1}. The structure of the band gap states is complicated (Figure 1) \cite{1}. The density of the conduction band states and the valence band states are \(N_c = 1.1 \cdot 10^{19} \text{ cm}^{-3}\) and \(N_v = 3.3 \cdot 10^{19} \text{ cm}^{-3}\) \cite{1}. Therefore IIa-type diamond \cite{1} has density of the conduction band states only 10 – 100 times higher than the density of the band gap impurity states.

![Figure 1. The structure of the band gap states of IIa type diamond: A, B\textsubscript{1}, B\textsubscript{2}, C, V, V' – are the legends of the energy states of various nitrogen defects. \cite{1}.](image-url)
The complicated structure of the band gap states makes possible the effects of polarization [3, 4] and quasi-two-photon absorption [5]. The last one is appeared when a photon of one wavelength throws a charge to the trap in the band gap, and another photon throws it into the conduction band. Moreover, each of the two photons has energy smaller than the band gap. It is appeared as sensitizing of the diamond photodetector to the emission with photon energy lesser than the band gap [5]. The relaxation time is tens of hours because the energy traps of nitrogen impurities are located deep (\(E_N \sim 2\) eV [5]) in the band gap. These trapped states were pumped at room temperature for several tens of pulses of UV laser with a wavelength of 266 nm and intensity of 250 mW/cm². This diamond detector demonstrated a time-dependent photosensitivity to emission of an optical parametric oscillator, which generated visible light for two days.

The last mentioned photosensitive feature of diamond provides both negative (the accuracy of the photometric measurements of the UV solar-blind range is strongly reduced) and positive effects on the diamond optoelectronic devices [6, 7]. The question of the pumping source power is issue of the day as well. The known studies of diamond sensitizing [5] were performed using a laser. We investigate the possibility of diamond detector to detect the low-power polychrome visible and near IR light.

2. Objects of the Research
We selected two diamond plates with different concentrations of nitrogen impurities as objects of the investigation. The diamond plate #1 has size of 3.2×2.5×0.3 mm and nitrogen concentration of \(C_N = 9.0 \times 10^{18}\) cm⁻³ (IIa type diamond). The diamond plate #2 has size of 2.9×2.3×0.3 mm and nitrogen concentration of \(C_N = 3.6 \times 10^{19}\) cm⁻³ (“transitional” type diamond). We produced two photodetectors using these diamond plates correspondingly. Figure 2 demonstrates the pattern of the detector (Figure 2).

![Figure 2. The pattern of the diamond photodetector: 1 – semitransparent platinum layer, 2 – diamond plate; 3 – aluminum electrical contact.](image)

3. The Experimental Setup
The experimental setup is demonstrated on the Figure 3. The optical condenser (2) directs UV light of the deuterium lamp (1) into monochromator (3) which directs the dispersed light to the diamond photodetector (4) (Figure 3). The preamplifier (8) amplifies and converts the photocurrent into a voltage which is fed into voltmeter (9). The setup allows illuminating of the diamond photodetector active area using a halogen lamp (5) broadband non-coherent radiation passing through the aperture plate (6) and the optical filter (7). By monochromator scanning of the deuterium lamp radiation we obtain the spectral dependencies of the diamond detector photosensitivity.
4. Experimental details and Discussion

We apply bias voltage of $V_{\text{bias}} = -100$ В to the diamond photodetectors #1 and #2 (Figure 2). Then we shortly time apply the light bias illuminating by the halogen lamp to the detector active area. The UV deuterium lamp is not used in this step of the experiment. As expected, the photocurrent is not generated when illuminating of the active detector area by the halogen lamp emission during both short time and several days as the lamp emits the light with wavelengths of more than 380 nm though the "red" optical limit of the type IIa diamond photosensitivity is about 230 nm. Probably, the relaxation rate of charge carriers at the impurity energy states equals to the generation rate of them using the halogen lamp emission.

We turn on the UV deuterium lamp and detect the spectral dependencies of the photosensitivity of the diamond detectors without the bias light application and with one. We obtain the dependencies of the photoresponse multiplicity ($I_{\text{photo}}/I_{\text{dark}}$) from the UV wavelengths (Figure 4). The photocurrent is intensively amplified when applied the light bias of the halogen lamp emission to the photodetectors (Figure 4, curves 2, 4). For the diamond detector #1 the photocurrent is amplified twice in the spectral range of the maximum photosensitivity ($\lambda = 220 – 227$ nm) and the increase is much smaller in the range ($240 – 340$ nm) which corresponds the photosensitive impurity energy states (Figure 4, curves 1 and 2). While, for the diamond detector #2 the photocurrent is amplified only 1.5 times in the $\lambda = 220 – 227$ nm spectral range and 2.5 times in the $\lambda = 240 – 340$ nm spectral range (Figure 4, curves 3 and 4). Such a different behavior of the photosensitivity spectral dependencies of two types of the diamond detectors is due to the difference in the mechanisms of the photocurrent amplifying in these spectral ranges as well as the different structure of the band gap impurity states of diamond.

Figure 3. The experimental setup: 1 – deuterium lamp, 2 – optical condenser, 3 – monochromator, 4 – diamond photodetector, 5 – halogen lamp, 6 – aperture plate, 7 – optical filter, 8 – preamplifier, 9 – voltmeter.

Figure 4. The dependencies of the photoresponse multiplicity from the UV wavelength for the diamond photodetectors:

the detector #1 – curves 1 and 2 correspond to the dependencies without application of the light bias broadband radiation of the halogen lamp and with one;

the detector #2 – curves 3 and 4 correspond to the dependencies without application of the light bias radiation and with one.
We assume that amplifying of the photocurrent in the spectral range of the maximum photosensitivity of a diamond is due to the charge carriers which are generated by the UV radiation in the valence band or the conduction band then partially trapped by the band gap impurity states. Some trapped charge carriers are thrown back from the band gap into the conduction band or the valence band when the broadband spectral light bias application. These charges generates additional the impurity photocurrent. The charge carriers throwing to the conduction band and valence band is possible due to the broadband spectral light bias and a lot of the band gap impurity states.

The mechanism of the photocurrent generation in the spectral range \(\lambda = 240 – 340\ \text{nm}\) of the band gap impurity states is different. In this case the UV radiation throws the charge carriers into the band gap states and then the light bias throws the charge carriers to the conduction band or the valence band. Therefore the differences become clear in the photoconductivity spectra of the IIa type diamond (Figure 4, curves 1 and 2) and the "transitional" type diamond (Figure 4, curves 3 and 4).

We assume that a lesser amplifying of the photocurrent at the maximum photosensitivity of the "transitional" diamond is caused by a decrease the mobility and lifetime of nonequilibrium charge carriers [1] due to a lot of the energy traps in the band gap. In addition there are a lot of the deep energy traps in the band gap of IIa diamond. Therefore the narrow UV radiation, which selected by the monochromator, does not throw sufficient amount of the charge carriers to the band gap states. The small amplifying of the photocurrent in the 300 – 340 nm spectral range (Fig 4, curve 2) indirectly confirms that the band gap impurity states are deeper in the IIa diamond in comparison with the “transitional” diamond.

We set up an experiment to determine the effect of the band gap states for the photosensitivity of these diamond detectors. Using the set of the light filters (Figure 5) which are established between the halogen lamp and the diamond detector we obtain the dependencies of photoresponse multiplicity \(I_{\text{photo}}/I_{\text{dark}}\) from the UV wavelengths (Figure 6) for the detector #2. We apply the broadband spectrum light bias of the halogen lamp to the diamond detector at the same time. The set of the SZS25 and SZS21 light filters passes visible light of the 380 – 560 nm range (Figure 5a). The light filter KC19 passes near infra-red spectral range of the halogen lamp radiation (Figure 5b).

![Figure 5. The transmission spectra of the light filters set (in correspond with [8])](image)
Figure 6. The dependencies of photoresponse multiplicity from the UV wavelength for the diamond detector #2: 1 – without the light bias application, 2 – with application of the light bias and the set of SZS25 and SZS21 light filters, 3 – with application of the light bias and the light filter of КС19; 4 – with application of the light bias without light filters.

The amplifying in the photocurrent in the spectral range of 240 – 380 nm indicates the distribution of the band gap impurity states. The “transitional” diamond has equally smeared-out density of the gap states (Figure 1). Therefore the amplifying in the photocurrent for application both the visible (Figure 6, curve 2) and near IR (Figure 6, curve 3) light bias is about the same and depends on both the filtered spectral bands (Figure 5) and the halogen lamp spectrum. Though there are some differences of the photoresponse spectra in the 280 – 380 nm range (Figure 6, curves 2 and 3) at application both the near IR and the visible light bias which are determined by density of the gap states. In order to study in detail the band gap states, it is necessary detect the spectral photosensitivity depending on the UV wavelength and at the same time scan the light bias emission of the halogen lamp by second monochromator. However, in the production of devices based on diamond, we need the knowledge of the integral dependencies of the influence of background illumination on the spectral photosensitivity of a diamond detector.

There is the interesting spectral range of 190 – 220 nm of the photosensitivity spectrum of the “transitional” diamond. While the detector #1 at the light bias application demonstrates a proportional amplifying in the actual photocurrent (Figure 4, curves 1 and 2), the diamond #2 does not demonstrate the photosensitivity in this spectral range without the light bias application (Figure 4, curve 3). Therefore, it is unclear, why is the photosensitivity take place at application of the safe light bias? The light bias application of the different spectral ranges (Figure 5), which are selected from the broadband spectral radiation of the halogen lamp, allows you to answer it.

Well known for semiconductors [9], there is a spectral flat-topped dependence of photocurrent in the range of wavelengths higher than the band gap absorption. This dependence is related to the fact that the charge carriers are thrown into the conduction band by a radiation with a higher energy than the band gap. Then the charge carriers rapidly relax to the bottom of the conduction band or to the top of the valence band and then generate a photocurrent. This dependence usually has a smooth slope [9, 10] from the band gap absorption toward shorter wavelengths. This slope is associated with increased optical absorption of the semiconductor with decreasing wavelength. Therefore penetration of the light emission into the semiconductor depth is reduced and hence photocurrent is weakening.

However, a diamond semiconductor has a strong slope of the photocurrent in the range of shorter wavelengths (λ < 220 nm) near the maximum photoresponse (in addition, the slope is slower for the diamond is impurities-free – the comparison of the curves 1 and 3 at Figure 5). This is due to a lot of nitrogen associated defects are displaced to the diamond surface. These defects are traps for charge carriers generated by light emission. Therefore the photocurrent is completely quenched for the “transitional” diamond into λ < 220 nm the spectral range (Figure 5, curve 3 and Figure 6, curve 1).
The application of the light bias and light filters set allows splitting the charge carriers which are trapped by the different energy states of the band gap. In the spectral range of $\lambda < 220$ nm the photocurrent is only amplified with the visible light bias application (Figure 6, curves 2 and 4) while as the near IR light bias application does not amplify the photocurrent into the spectral range (Figure 6, curve 3). Consequently there are not shallow states of the band gap on the surface of the “transitional” diamond. Therefore the charge recombination takes place at deeper states of the band gap.

5. Conclusion
To produce high stability operational devices based on diamond photodetectors it is necessary to apply best possible of clean impurities diamonds. During operation of such devices must be considered the effect of background lighting on the photosensitivity of the detector, in spite of the diamond photodetector is a solar-blind (insensitive to visible and infrared light emission) without UV illumination as well.

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