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Photo-response performance regulation of a type-Ib diamond-based photodetector by H₂ annealing and ozone treatment†

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Deep ultraviolet (DUV) photodetectors (PDs) based on ultra-wide bandgap semiconductor diamond-based have attracted extensive attention due to the immunity to solar light on the earth and thermal stability in extremely harsh environments. However, the preparation of a high-quality and high-purity single-crystal diamond epilayer remains a major obstacle to achieve high photo-response performance. Here, we demonstrate that diamond PDs with tunable photoresponse properties can be obtained on type-Ib diamonds through simple annealing in ambient H₂ and a surface ozone treatment process. The surface holes and the nitrogen defects inside the type-Ib diamond work together to regulate the overall photoresponse performance. The responsivity of the PDs can be adjusted from 84.3 A W⁻¹ to 2.65 × 10⁴ A W⁻¹, and the response time can be modulated from 42.5 s to less than 240 ms. The achievement of photo response performance modulation of PDs originates from the cooperative effect of deep natural nitrogen defects and surface states. Thus, our findings provide an alternative method and facile strategy for the tailoring of PDs' performance, which can meet different application requirements.

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Introduction

A solar-blind deep-ultraviolet (DUV) photodetector exhibits excellent spectral selectivity since it responds to light with wavelengths shorter than 280 nm, which is almost non-existent in the earth's atmosphere.^{1–3} The extremely low noise interference from the environment enables high-accuracy detection of solar-blind DUV light. Thus, solar-blind DUV PDs are in demand for applications covering intersatellite secure communications,⁴ DUV imaging,⁵ and environmental monitoring and analysis.^{6–8} Diamond is a single-element ultra-wide bandgap (5.5 eV) semiconductor, which has an excellent thermally and chemically stable structure, the highest thermal conductivity (22 W cm⁻¹ K⁻¹), and a large breakdown field > 10 MV cm⁻¹.^{9–12} Compared with multi-element compound semiconductors, such as AlGaN, Ga₂O₃, and MgZnO, diamond does not have problems such as component segregation or oxygen vacancies.^{13–16} Besides, diamond has high radiation resistance.¹⁷ Furthermore, diamond can achieve high sensitivity to DUV light, but weak

response to visible light, making it an extremely attractive material for preparing solar-blind DUV PDs.

The initial efforts in developing diamond PDs were mainly on polycrystalline diamond. In 1993, Binari *et al.* fabricated a metal-semiconductor-metal (MSM) PD based on polycrystalline diamond, which showed a quantum efficiency of 39% at 400 V bias voltage and under a wavelength of 200 nm.¹⁸ In 1998, Jiang *et al.* demonstrated an MSM PD based on diamond thin film grown on a silicon substrate, which achieved a low operating voltage around 5 V.¹⁹ In 2005, we investigated the performance of a PD based on boron (B)-doped homoepitaxial single-crystal diamond (SCD), which showed a high ultraviolet photocurrent at 220 nm (seven orders of magnitude higher than dark current) and a high spectral selectivity (DUV/visible rejection ratio of 10⁶).²⁰ Lin *et al.* developed SCD MSM PDs, which showed a responsivity of 21.8 A W⁻¹ and a detectivity of 1.39 × 10¹² cm Hz^{1/2} W⁻¹ at 218 nm light.²¹ A responsivity of 524.9 A W⁻¹ was later achieved by treating the SCD epitaxial layer with hydrogen plasma and optimizing the Schottky barrier with an electrode contact.²² To date, almost all high-performance diamond-based solar blind DUV PDs rely on high-quality epitaxial layers. Recently, we showed an EQE of 9.41 × 10⁶% for the diamond DUV PDs by simply treating a type-Ib diamond substrate using hydrogen plasma treatment.²³ Regardless of the growth of high-quality epitaxial layers or hydrogen plasma treatment, MPCVD equipment was used in our previous work.

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In this work, we report the development of DUV detectors by simply annealing type-Ib diamond substrates in an ambient H_2 . By combining with UV/ozone treatment, the overall response properties such as the DUV responsivity, response speed, dark current, and spectral response of the diamond PDs can be regulated. The responsivity (R) of the PD based on hydrogen-annealed diamond is up to $2.65 \times 10^4 \text{ A W}^{-1}$, corresponding to an ultrahigh external quantum efficiency (EQE) of $1.50 \times 10^7\%$ but a lower response speed. After UV/ozone treatment, the device response time can be as short as less than 240 ms. The modulation of the photoresponse properties of the H-annealed type-Ib diamond is resulted from the cooperative effect of the nitrogen impurity in diamond and the surface states. These findings provide a simple and effective strategy for fabricating diamond DUV PDs, which can meet different application requirements.

Results and discussion

Material characterization

The surface morphology of the H_2 annealed type-Ib diamond substrate scanned by AFM is shown in Fig. 1(a1) and (a2). It can be seen that the surface of diamond is smooth without large bulges or damage after H_2 annealing. The root mean square (RMS) is extremely low ($\sim 0.04 \text{ nm}$). Fig. 1(b1 and b2) display the 2D mapping of the Raman peak full width at half maximum (FWHM) of an area of $30 \times 30 \mu\text{m}^2$ and the statistical histogram, respectively. The Raman peak position is around 1332.23 cm^{-1} , which is close to the standard value of 1332.5 cm^{-1} . The FWHM is evenly distributed, and the average FWHM is around 2.1 cm^{-1} . Based on the XPS analysis shown in Fig. 1(c1) and (c2), for hydrogen annealed diamond, the C-C sp^3 components account

for 96.3% and C-O accounts for 3.7%. The peak of C-O is attributed to the surface adsorbed carbon oxides when exposed in ambient air.^{24,25} After 10 min ozone treatment, the content of C-O increases to 5.87%, indicating that its surface gradually changes from hydrogen terminal to oxygen terminal. Furthermore, the sp^3 C-C peak of ozone treated diamond shifts from 282.25 eV to 283.96 eV, which can be explained by the difference of band bending.^{26,27}

Photoresponse property regulation

The surface electrical conductivity of H-terminated diamond can be enhanced by hydrogen annealing. Taking into account that the bulk type-Ib diamond contains a large amount of nitrogen (N) around 10^{19} cm^{-3} , the surface electrical conductivity caused by two-dimensional hole gas (2DHG) is decayed because of the depletion of partial surface holes due to N trapping, which is similar to hydrogen plasma treated surfaces. The as-annealed diamond-based PD has a dark current around $2.37 \times 10^{-5} \text{ A}$ at 5 V, as shown in Fig. 2(a). This value is two orders of magnitude lower than that of "intrinsic" diamond with surface H-termination.²⁸ The dark current of the PD ozone treated for 5 minutes is reduced around $3.82 \times 10^{-8} \text{ A}$, and that of the PD ozone treated for 10 minutes is around $1.75 \times 10^{-9} \text{ A}$, as depicted in Fig. 2(b) and (c), respectively. Under 220 nm DUV light illumination, the photocurrent of three PDs is enhanced to $1.10 \times 10^{-4} \text{ A}$, $3.51 \times 10^{-6} \text{ A}$, and $2.76 \times 10^{-7} \text{ A}$, respectively, illustrating a sensitive response to DUV light. The PD's dark current and photocurrent gradually decrease with prolonged ozone treatment durations (Fig. 2(d)), resulting from the decrease of the 2DHG concentration. And the ratio of photocurrent to dark current (PDCR) of the PDs increases with the ozone treatment time.

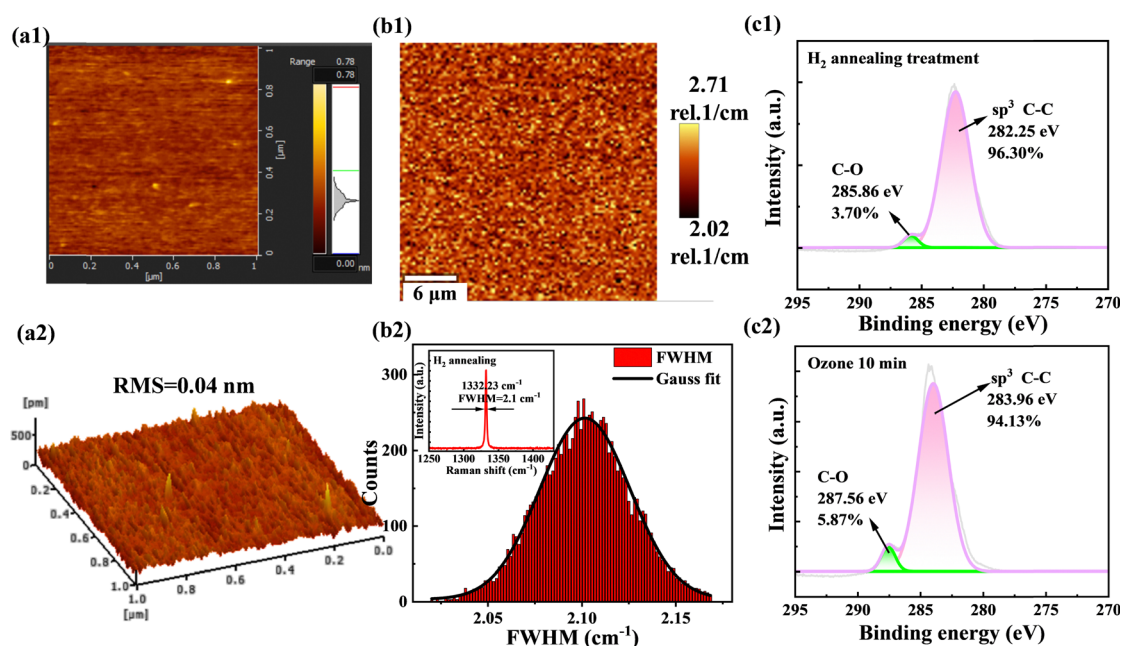


Fig. 1 (a1) and (a2) 2 dimensional (D) and 3D surface morphology of H_2 annealed diamond. (b1) and (b2) Raman imaging of an area of $30 \times 30 \mu\text{m}^2$, and statistical distribution of the Raman FWHM of the H_2 annealed diamond. (c1) and (c2) X-ray photoelectron spectroscopy (XPS) spectra of H_2 annealed and 10 min ozone-treated diamond.



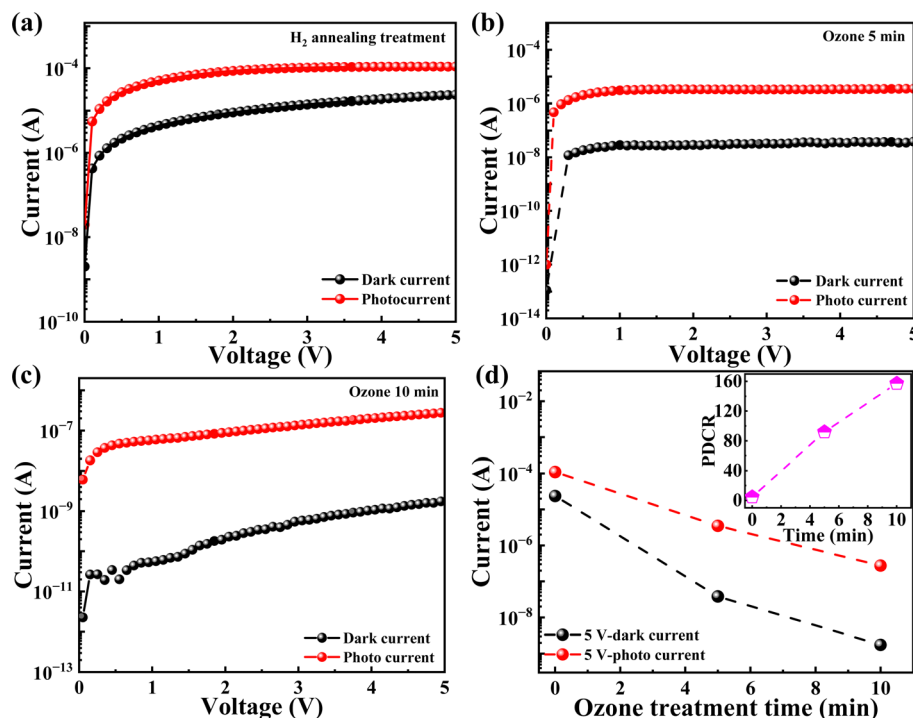


Fig. 2 *I*–*V* characteristics of the diamond PDs. (a) H₂-annealed, (b) ozone treatment for 5 min, (c) ozone treatment for 10 min. (d) Dark and photo current vs. ozone treatment time.

The responsivity (*R*) and external quantum efficiency, EQE, critical figures-of-merit in photodetectors, representing the ratio of extracted carriers and incident photons, are obtained under 5 V bias. The responsivity, *R*, is calculated according to:

$$R = \text{EQE} \frac{e\lambda}{hc}$$

where *e*, *λ*, *h*, and *c* are electron charge, incident light wavelength, Planck constant, and light speed, respectively.^{29–31} The PDs exhibit higher EQE in the DUV region and lower EQE in the visible region. By using the optically active area of $5 \times 10^{-4} \text{ cm}^2$ and the power density ($6.50 \mu\text{W cm}^{-2}$) of the 220 nm light, the responsivity of $2.65 \times 10^4 \text{ A W}^{-1}$ is obtained, corresponding to an EQE of $\sim 1.50 \times 10^7\%$ for the H₂-annealed PD, as shown Fig. 3. Meanwhile, the EQEs of the PD with 5 min and 10 min UV/ozone treatments are $6.00 \times 10^5\%$ and $4.76 \times 10^4\%$, respectively, corresponding to the responsivity of $1.06 \times 10^3 \text{ A W}^{-1}$ and 84.3 A W^{-1} , respectively. The cut-off wavelength shifts rightward to 270 nm because the presence of a large amount of nitrogen (N) doping inside the HPHT diamond will enhance light absorption to promote photocurrent.^{32,33} The detectivity, *D*^{*}, is determined by noise current *I*_n, responsivity *R*, illumination area *A*, and the bandwidth *B*,^{34,35} which is expressed by:

$$D^* = \frac{R\sqrt{AB}}{I_n}$$

The noise currents of the H₂ annealed PD, the 5 min ozone-treated PD, and the 10 min ozone-treated PD are $3.11 \times 10^{-7} \text{ A Hz}^{-1/2}$, $2.65 \times 10^{-9} \text{ A Hz}^{-1/2}$, and $3.09 \times 10^{-11} \text{ A Hz}^{-1/2}$, respectively, as illustrated in Fig. 3(c). Based on the noise current,

D^{*} can be calculated to be $6.03 \times 10^9 \text{ cm Hz}^{1/2} \text{ W}^{-1}$, $2.83 \times 10^{10} \text{ cm Hz}^{1/2} \text{ W}^{-1}$, and $1.93 \times 10^{11} \text{ cm Hz}^{1/2} \text{ W}^{-1}$ for the H₂ annealed PD, the 5 min ozone-treated PD, and the 10 min ozone-treated PD, respectively, as shown in Fig. 3(d). The PD with 10 min ozone treatment has a higher *D*^{*}, attributed to the lower noise current. And all PDs exhibit higher *D*^{*} in the DUV region.

Furthermore, the response time including the rise time *τ*_r (10% to 90% of the maximum photocurrent) and the decay time *τ*_d (90% to 10% of the maximum photocurrent) were calculated. The *τ*_r and *τ*_d of H₂ annealed PD are beyond 42 s (Fig. 4(a)), and the response time becomes shortened with the prolonging of the ozone time (Fig. 4(d)). The PDs with 5 min ozone and 10 min ozone treatment have the response time of *τ*_r/*τ*_d = 9.50 s/12.24 s, and *τ*_r/*τ*_d < 240 ms, respectively, as displayed in Fig. 4(b) and (c), respectively. The PDs show no current decay for cyclic switching, indicating that the PDs have good stability, as shown in Fig. S2 (ESI†). Furthermore, the photocurrent increases linearly with the incident power density.

The key parameters including the dark current, *R*, EQE, and response time of diamond-based PDs in this work and previously reported work^{22,23,36–42} are summarized in Table 1. Almost all other reported diamond PDs in the table are based on epitaxial SCD layers prepared using the MPCVD method. Our other work²³ demonstrated an EQE of $9.41 \times 10^6\%$ by using MPCVD hydrogen plasma to treat a type-Ib diamond surface. In this work, we simply used H₂ annealed commercial HPHT type-Ib diamond to achieve comparable ultrahigh responsivity ($2.65 \times 10^4 \text{ A W}^{-1}$) and external quantum efficiency ($1.50 \times 10^7\%$). Furthermore, the PDs in this work operate with a voltage as low as 5 V and the response



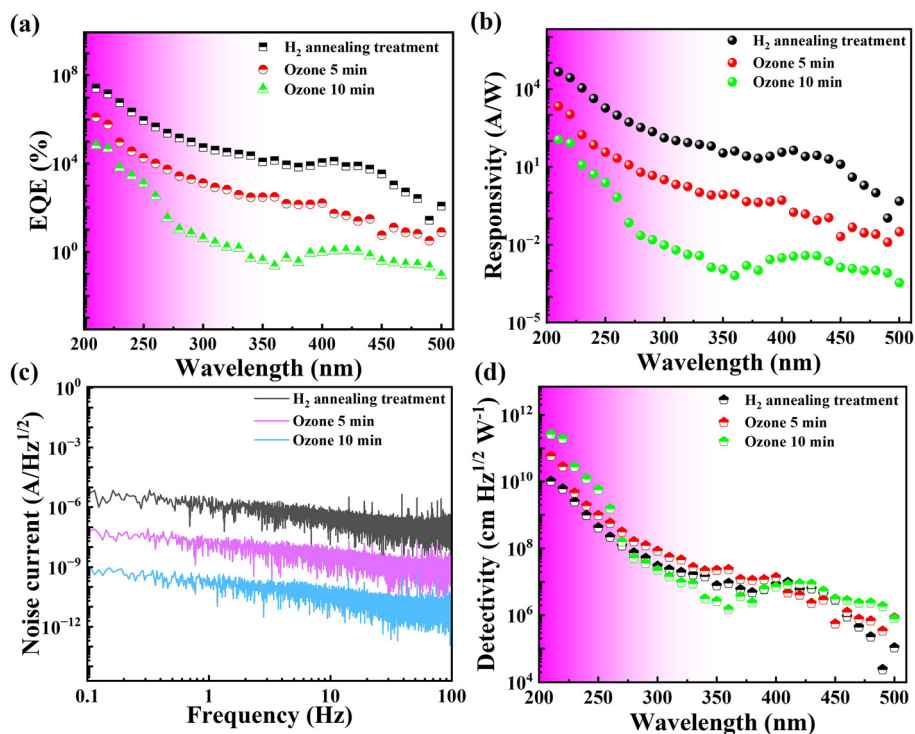


Fig. 3 (a) The measured external quantum efficiency, EQE, (b) responsivity, R , (c) noise current, and (d) detectivity, D^* of PDs.

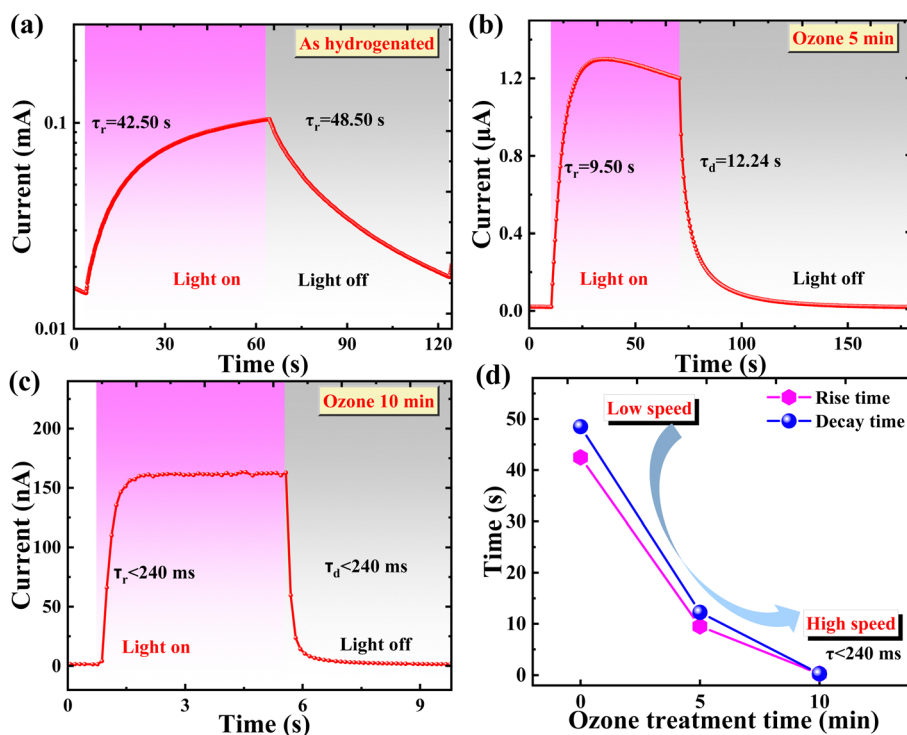


Fig. 4 Time-dependent photo-response of PDs. (a) H_2 -annealed, (b) ozone-treated for 5 min and (c) ozone-treated for 10 min. (d) Response time vs. ozone treatment time.

performance of the PDs can be tailored through surface treatments. The surface conductivities and photoresponse properties for the diamond surfaces either by hydrogen plasma

treatment or thermal annealing in a hydrogen ambient are similar. The thermal stability of the diamond surfaces treated by these two methods is under investigation.



Table 1 Comparisons of the photodetection performances of Ga₂O₃-based photodetectors

Material	Structure	Dark current	Responsivity (A W ⁻¹)	EQE (%)	Response time (τ _r /τ _d)	Ref.
B-doped SCD	MSM	10 ⁻¹² A@30 V	18@-23 V, 220 nm	1.01 × 10 ⁴	<10 ms	36
SCD	MSM	1.12 × 10 ⁻¹² A@30 V	0.20@30 V, 220 nm	1.12 × 10 ²	20 μs/1000 μs	37
Graphene-MCD	Heterojunction	10 ⁻⁶ A cm ⁻²	1.4@5 V, 220 nm	7.9 × 10 ²	—	38
SCD	MSM	10 ⁻¹² A@30 V	1.18@50 V, 210 nm	6.66 × 10 ²	640 ms/34 ms	39
SCD	MSM	10 ⁻¹³ A@50 V	0.11@7 V, 220 nm	62.1	—	40
SCD	MSM	1.08 × 10 ⁻¹⁰ A@13 V	524.9@13 V, 220 nm	2.96 × 10 ⁵	0.16 μs/120 μs	22
SCD	MSM	10 ⁻¹² A@47 V	0.013@47 V, 225 nm	7.19	5 ns/20 ns	41
SCD	MSM	10 ⁻¹² A@30 V	0.325@30 V, 210 nm	1.92 × 10 ²	1.2 ms	42
H-plasma treated Ib-diamond	MSM	2.34 × 10 ⁻⁵ A@5 V	1.6 × 10 ⁴ @5 V, 220 nm	9.41 × 10 ⁶	30.4 s	23
H ₂ annealed Ib-diamond	MSM	2.37 × 10 ⁻⁵ A@5 V	2.65 × 10 ⁴ @5 V, 220 nm	1.50 × 10 ⁷	42.5 s/48.5 s	This work
Ozone 5 min Ib-diamond	MSM	3.82 × 10 ⁻⁸ A@5 V	1.06 × 10 ³ @5 V, 220 nm	6.00 × 10 ⁵	9.50 s/12.24 s	This work
Ozone 10 min Ib-diamond	MSM	1.75 × 10 ⁻⁹ A@5 V	84.3@5 V, 220 nm	4.76 × 10 ⁴	<240 ms	This work

Photoresponse mechanism

Hydrogen-annealed type-Ib diamond shows a negative electron affinity (NEA) and exhibits surface conductivity due to the formation of two-dimensional hole gas on the surface.^{43–45} Thus, the energy band of H₂ annealed diamond bends upwards. Furthermore, there are nitrogen defects inside the type Ib-diamond, which compensate surface holes and electrons and result in an increase in ionized N⁺ traps, as shown in Fig. 5(a). This results in the H₂-annealed type-Ib diamond PD possessing lower dark current (2.37 × 10⁻⁵ A) than those of H-terminated intrinsic diamonds (~mA).^{46,47} After ozone treatment, the surface conductivity and surface hole concentration decrease, the energy band bends upward slightly, and less nitrogen is ionized, as shown in Fig. 5(b) and (c). Under DUV illumination, the electrons in the valence band are excited

to the conduction band, and some of the electrons are captured by N⁺ traps, causing equivalent holes to accumulate near the surface and the energy band to bend upward more sharply, as shown in Fig. 5(d). This corresponds to the ultrahigh EQE (1.50 × 10⁷%) and responsivity (2.65 × 10⁴ A W⁻¹). While the regulation process of more N⁺ traps slows down the overall carrier recombination process, the response time of the H₂-annealed type-Ib diamond PD is longer (τ_r/τ_d = 42.50 s/48.50 s). As the UV/ozone treatment time increases, surface holes and N⁺ traps decrease, as depicted in Fig. 5(e) and (f), resulting in a lower EQE of 6.00 × 10⁵% and 4.76 × 10⁴%, respectively for the 5 min and 10 min ozone-treated PDs. And the carrier recombination gradually changes from being dominated by N⁺ traps to being dominated by band-to-band. Therefore, the response speed accelerates (τ_r/τ_d < 240 ms for 10 min ozone-treated PD).

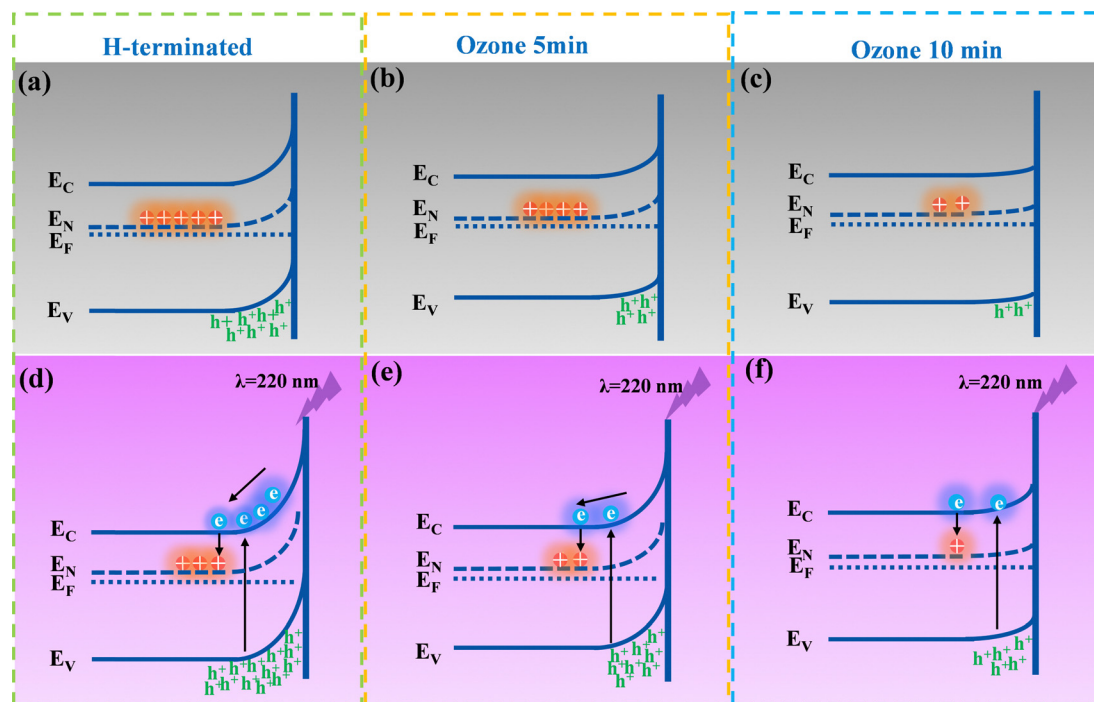


Fig. 5 Energy band diagrams of H₂-annealed, ozone-treated 5 min, and ozone-treated 10 min PDs: (a)–(c) in the dark condition and (d)–(f) under 220 nm UV light.



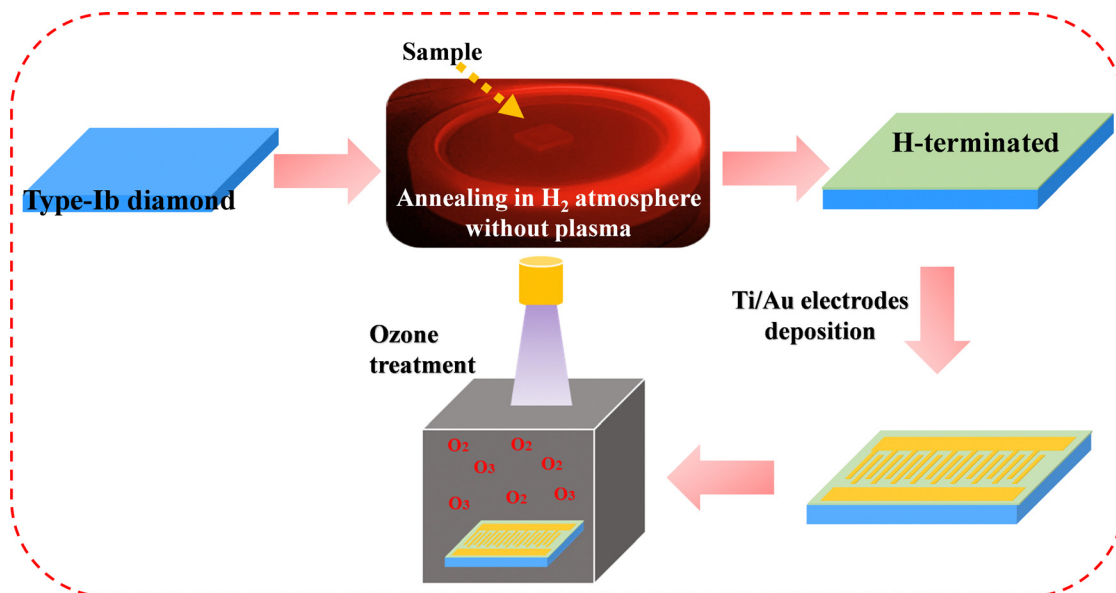


Fig. 6 Schematic diagrams of the experimental treatment route.

Experimental

The type Ib-type diamond with the dimensions of 2.5 mm × 2.5 mm × 0.5 mm was cleaned ultrasonically in acetone, absolute ethanol, and deionized water for 5 minutes, respectively. Before annealing in ambient H₂, the diamond substrate was boiled in an acid mixture of H₂SO₄ and HNO₃. The overall experimental treatment route is shown in Fig. 6. The cleaned diamond was transferred to a high-vacuum chamber, which has a base pressure of 10^{−7} Torr. The annealing temperature, the pressure, and the duration were 860 °C, 80 Torr, and 1 h, respectively. The Ti/Au interdigitated electrodes with a finger width of 10 μm were deposited on a hydrogen annealed diamond surface. The optically active receiving area is around 5 × 10^{−4} cm². The as-annealed PDs were placed into a UV/ozone reaction chamber for 5 min and 10 min treatments. The optical image of the PD is shown in Fig. S1 (ESI†). The diamond surface morphology and root mean square were characterized by atomic force microscopy (AFM). The Raman spectrometer with a 532 nm laser was used to measure the crystal quality of the as-annealed diamond. A commercial X-ray photoelectron spectrometer (XPS, Thermo Fisher Scientific, Japan) was used to measure the binding states of the surface composition. The overall photoelectric performance of the PDs was measured by using a Keithly2400 semiconductor Analyzer and an Ushio Xenon lamp combined with an Acton monochromator with order sorting filters and a standard lock-in amplifier technique. The power density of the 220 nm incident light is around 6.5 μW cm^{−2}.

Conclusions

In conclusion, a high-temperature annealing procedure in ambient H₂ was conducted to fabricate a H-terminated type-Ib diamond-based PD. The surface characteristics and the overall photoresponse performance of H₂ annealed type-Ib

diamond are comparable with those of hydrogen plasma-treated type-Ib diamond. The UV/ozone surface treatment regulated the photoresponse performance through the cooperation of surface states and the natural doped nitrogen in type Ib diamond. The responsivity was modulated from 2.65 × 10⁴ A W^{−1} to 84.3 A W^{−1} and the response time from 42.5 s to <240 ms. These findings provide a simple and effective technique to fabricate DUV-PDs with tunable performance for different industrial applications.

Data availability

The authors confirm that the data supporting this article have been included in the article or ESI.†

Conflicts of interest

The authors declare that they have no conflict of interest.

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