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Photoinduced effects in field electron emission from diamond needles

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We report an explicit experimental observation of photostimulated electron field emission from diamond. The electron emission properties of monocrystalline diamond needles were investigated in the dark and under illumination by nanosecond laser pulses. A prominent increase in the electron emission current was detected under illumination by light with photon energies above 5.0 eV. The linear dependence of the photoinduced emission current on the light intensity was observed in the spectral range of 5.0 to 5.9 eV, while its field dependence demonstrated saturation behavior. The remarkable feature of the observed phenomenon was the fact that illuminated and field emission areas of the diamond needles were spatially separated by about 100 μm in the used experimental setup. Possible mechanisms for the observed effects are discussed. *Published by AIP Publishing.*
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Cold cathodes based on electron field emission (FE) are attractive for numerous applications including vacuum sensors,[1] electron sources used in electron microscopes,[2] and portable X-ray sources.[3] Combination of electron emission capabilities with photosensitivity of semiconducting materials allows creation of light controlled high brilliant electron sources.[4–6] Due to general principles of vacuum electronic device design, it is highly desirable to have illumination of the optically driven cathodes from its back side and electron emission forward to an extracting electrode. Reasonable intensities of photostimulated electron emission are expected for cathode materials possessing combination of very special properties, including sustainability to the action of the strong electric field and ion bombardment, large light absorption depth, and free path of photo-excited charge carriers.[7] From this point of view, diamond looks as an ideal candidate offering potential ability for creation of the optically driven cathodes due to its wide band gap, high thermal conductivity, chemical inertness, and mechanical stability.[8] In this paper, we report the study of the photosensitivity of field electron emission from single crystal diamond needles serving as a robust point cold cathode.

Single-crystal diamond needles were produced in a two-step process including the growth of polycrystalline (100)-textured diamond films by chemical vapour deposition (CVD) and subsequent selective thermal oxidation of thus obtained films. With properly chosen parameters of the CVD process, the as grown films were composed of needle-like diamond single crystals of more than 100 μm in length, incorporated into a less ordered material constituted of nanometer sized diamonds and disordered carbon. The oxidation temperature was chosen to provide selective gasification of all film components except for large needle-like crystals. Details of the employed processes and characteristics of produced diamond needles are described elsewhere.[9,10] Individual diamond needles of about 120–160 μm in length were extracted from oxidized films and mounted on the holders fabricated from n-doped Si wafers that were thinned to about 200–250 μm thickness by mechanical grinding. The central parts of the $5 \times 5\,\text{mm}^2$ holders were mechanically dimple grinded to provide a spherical recess with a diameter of about 3.5 mm and a minimum remaining thickness of Si in the center of the recess of about 50 μm. Finally, holes of about 5 μm diameter were prepared in the thinnest part (i.e., in the middle of the spherical hollows) using a focused ion beam (FIB, Helios DualBeam NanoLab 450S, FEI Co., The Netherlands). The individual diamond needles were mounted on the holes using an *in-situ* micromanipulator, mechanically fixed and electrically connected by electron-beam assisted Pt deposition. Fig. 1 represents scanning electron microscopy (SEM) images of the apex and the back side of a diamond needle fixed in the hole of a Si holder. A more detailed description of the process can be found in the supplementary material (Figs. S1–S5).

The electron emission from the needles was measured in an ultra-high vacuum (UHV) system, maintaining a residual gas pressure below 10^{-7} Pa.[11] The measurements were made in a diode configuration with a polished flat metallic Al anode (see Fig. S6 and S7 in the supplementary material). A mica plate with 40 μm thickness and a circular opening of 2.2 mm in diameter was centered at the position of the diamond needle, thereby providing a well-defined vacuum gap between the apex of the needle (cathode) and the metallic

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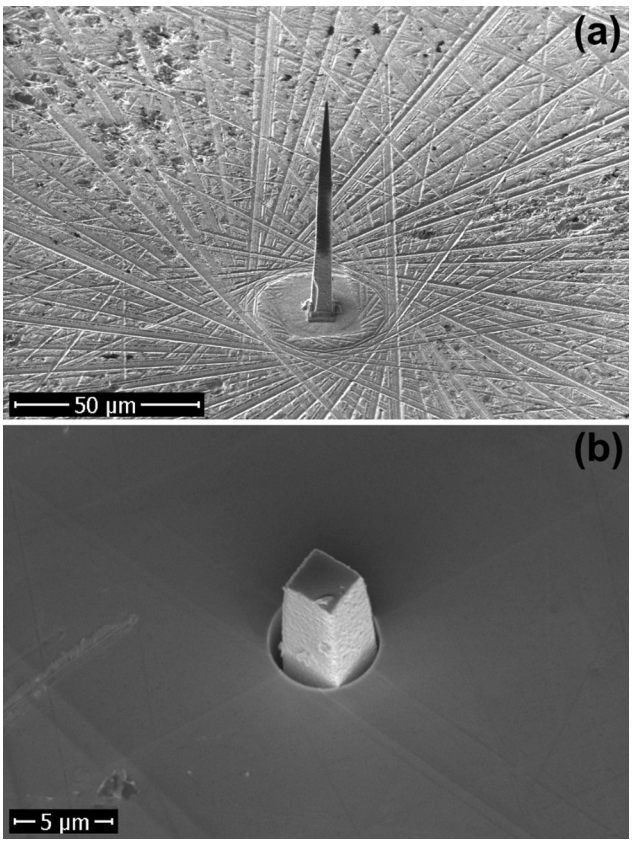

FIG. 1. Scanning electron micrographs of an individual diamond needle fixed in the Si holder from (a) the apex side and (b) from the back side.

anode. Due to the 50 μm thickness of the Si wafer around the diamond needle and high light absorption coefficients of silicon[12,13] and platinum,[14] the wafer itself was completely opaque for the optical radiation in the ultraviolet (UV) spectral range from about 210 nm to 400 nm (corresponding to ca. 5.9 eV to 3.1 eV photon energy) used in this study. The height of the needles above the wafer was in the range of 65 to 95 μm. The apex diameters of different needles varied from 50 to 250 nm as evidenced by SEM measurements. These geometrical parameters were used for the estimation of the local electric field (E_{local}) at the apex in comparison with its macroscopic value ($E_{macro} = V/d$) determined by the applied voltage (V) and the gap between the cathode and anode (d). The numerical calculations using COMSOL® indicate that the field enhancement factor $\beta = E_{local}/E_{macro}$ amounts to $\beta \approx 400$ at the apex for mentioned geometrical parameters in assumption of small penetration of the field into the needle (see Fig. S7 in the supplementary material).

To study the photostimulated emission, the back side of the Si holder with a diamond needle was illuminated by a pulsed tunable Nd:YAG laser (EKSPLA NT342A-SH). The laser was operated in a pulse power density range not higher than 200 kW/cm^2, which is well below the silicon ablation threshold (~400 MW/cm^2, Ref. 15). The pulse duration time and the repetition rate of the laser were 3.5 ns and 10 Hz, respectively. The laser beam was focused to the spot size between 1.2 mm und 2 mm, and the illumination was monitored by means of a pyroelectric sensor (Ophir Photonics PE10-C). All measurements were performed at room temperature. To exclude possible laser heating of the sample, 405 nm continuous wave (cw) radiation of a laser diode was used for comparative studies (see the supplementary material).

Reproducible current-voltage characteristics (I-V curves) for the electron emission from the diamond needles (see Fig. 2(a)) were measured after a preceding activation of the cathodes; the latter was achieved by a few voltage sweeps in the range of 1100–1600 V. These measurements were made in the dark without laser irradiation. In contradiction to similar measurements,[10] only a relatively small hysteresis between up and down cycles was detected for emission currents above 1 nA. After the activation, the onset voltage for 1 nA emission current was 675 V, corresponding to a macroscopic field of $E_{macro} = 3.97$ MV/m. The maximum current value during activation was around 120 nA at 1970 V. The current stability was typically better than 3% for a voltage below 1000 V. A weak irregular switching between discrete current levels was detected similar to that observed in field emission of carbon nanotubes, for example.[16] As can be seen

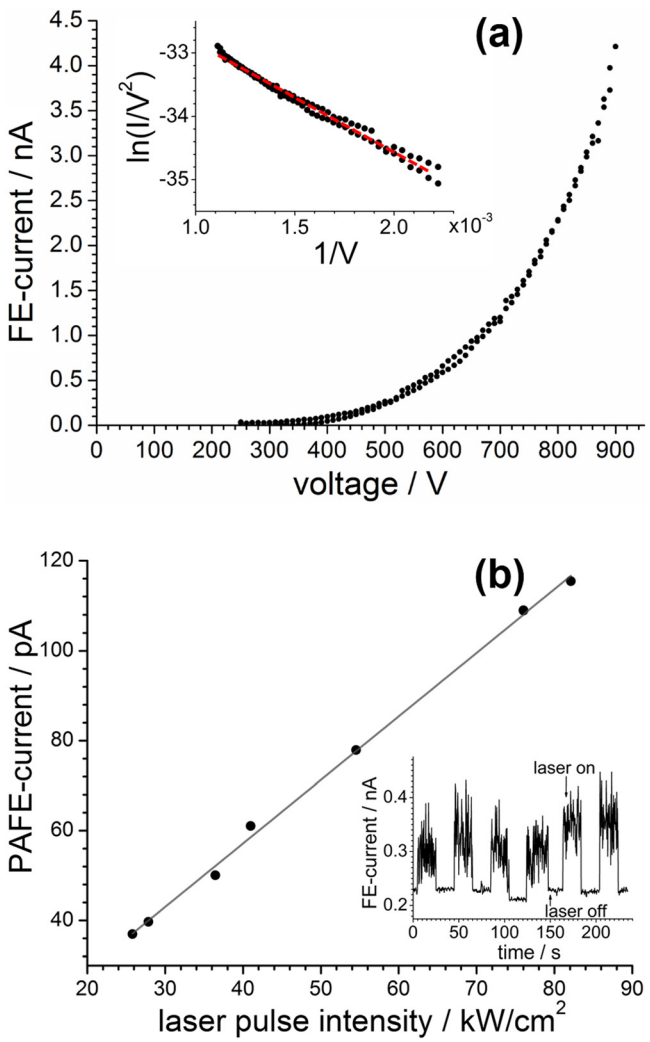

FIG. 2. Current-voltage characteristics of electron emission obtained from a diamond needle after activation in the dark (a) and dependence of the PAFE-current on the laser pulse intensity for an applied cathode potential of 500 V and a photon energy of $h\nu = 5.9$ eV (b). In the inset (a), the Fowler-Nordheim representation of the data is shown, and a linear fit of experimental data is highlighted by a dashed red line. The inset (b) shows the effect of alternating switching on and off the laser light source and the stability of the emission current with time. The pronounced fluctuation of the FE-current in the on state corresponds to the fluctuation of the laser power.

in the inset of Fig. 2(a), plotting of the I-V curves in Fowler-Nordheim (FN) coordinates demonstrates a linear dependence which is expected for field emission and obeys the FN law $I \propto E_{macro}^2 \exp(-B\varphi^{3/2}/E_{macro})$ derived for metallic emitters (where B is the specific constant and ϕ is the work function).[17]

Bulk diamond is known as a wide band gap material with almost negligible intrinsic conductivity as low as 10^{-20} S/cm.[18] Thus, the observed electron emission without illumination may only be explained by transport of electrons via additional states in the band gap corresponding to structural defects or dopants in the diamond needle.[19] This mechanism is expected to be especially efficient for the needles with relatively large surface areas containing numerous defects and impurities. Since the diode configuration should be operated without pre-annealing, the surface conductivity appeared to be high enough to prevent a possible saturation of the FE-current, which might occur for FE-currents even below 1 nA.[10]

Back-side illumination of the diamond needles by pulsed laser radiation led to a pronounced increase in the emission current. As can be seen in the inset in Fig. 2(b), the illumination of the back side of the cathode by 5.9 eV photons (210 nm wavelength) leads to a substantial increase in the emission current for an applied voltage of 500 V. In these experiments, trains of 3.5 ns laser pulses were switched on and off every 20 s. The time resolved current measurements using a 2 GHz oscilloscope, which were limited by the capacitance of the cable to ~10 ns, showed that the length of a single current pulse was roughly equal to the length of the laser pulse. The difference between the average emission current under illumination and in the dark, which we will further refer to as photo assisted field emission current (PAFE-current), correlated with the average laser intensity. It should be noted that the measured laser intensity fluctuated with time, and Gaussian distributions were observed for both laser intensity at every wavelength used in the experiments and emission current measured under illumination. The variation of measured PAFE-current was between 7% and 20%.

The PAFE-current turned out to be linearly depended on the light power as shown in Fig. 2(a) for $h\nu = 5.9$ eV. This result is representative for different values of the photon energies applied in our experiment and is intuitively expected for linear absorption processes in semiconductors.[20,21] It should be noted that the occurrence of nonlinear absorption effects in diamond, e.g., two- or three-photon absorption, is possible only for a significantly higher laser power of >25 GW/cm^2 than used here.[22,23]

The PAFE-current was found to be dependent on the photon energy of the laser radiation. This dependence is discussed herein in terms of photoresponsivity (R),[24] which may be expressed in our experiment as

$$R = \frac{I_P}{S \times W_l}, \tag{1}$$

where I_P is the PAFE-current (averaged taking into account the integration time of the picoamperemeter of 0.1 s and the pulse duration), W_l is the laser pulse intensity on the surface of the sample (taking into account the transmission characteristics of the beam splitter, the lens, and the vacuum window), and S is the area of the laser spot centered on the diamond needle on the back side of the Si holder. This area was estimated by the size of the illuminated area of the needle (30 μm^2 ± 20%) shown in Fig. 1. The experimentally measured dependence of photoresponsivity on photon energy is presented in Fig. 3(a).

As can be deduced from Fig. 3(a), the measured photoresponsivity has its maximum value of around 41.7 mA/W for the highest photon energy (5.9 eV) used. Decreasing the photon energy leads to a rapid decrease in R by three orders of magnitude, reaching the detection limit of our experimental setup at $h\nu = 4.0$ eV. The first-order derivative magnitude (see the inset of Fig. 3(a)) for the experimental data between 4.1 and 5 eV photon energy roughly remains constant around 3.5 mA/(W eV). A significant increase in the derivative by a factor of 4 is observed for $h\nu$>5 eV, where substantially larger photoresponsivities were measured. Having in mind that R is directly linked to the optical absorption,[25] the observed effect might be related to the fundamental absorption edge of diamond at 5.26 eV for 300 K[26] and the absorption increase for higher energy.

For a known value of R, the absorption coefficient may be obtained by the constant photocurrent method (CMP).[27,28]

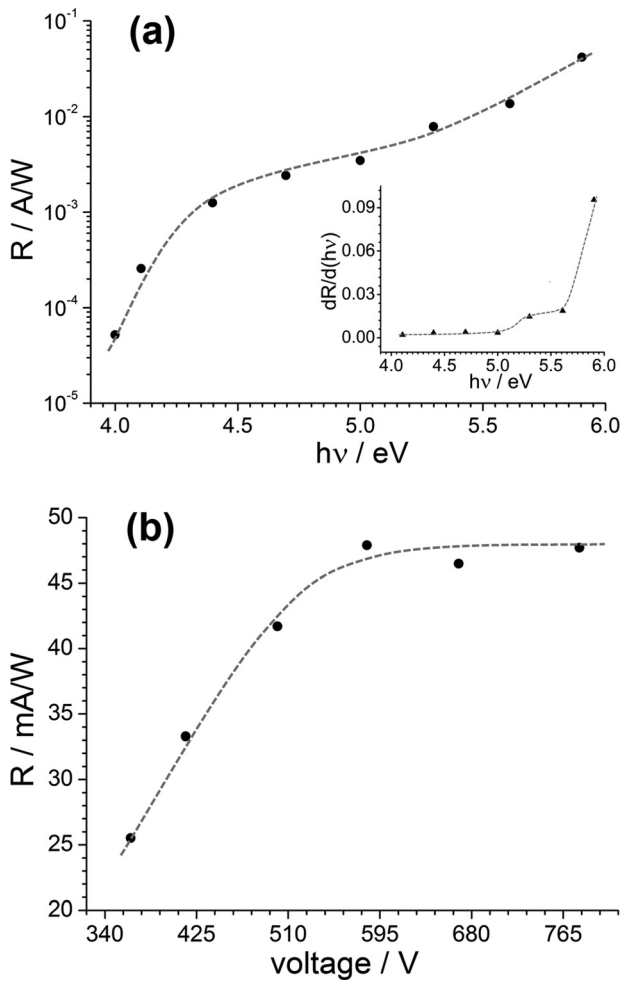

FIG. 3. Photoresponsivity, R, vs. photon energy, $h\nu$, for the back-illuminated diamond needle at an applied constant voltage of 500 V (a) and vs. applied voltage for $h\nu = 5.9$ eV and $W_l = 73$ kW/cm^2 (b). The inset (a) shows a simple forward first-order derivative of the data. The dashed lines are guides to the eye.

It was rather difficult to keep I_p constant in our experimental setup. Nevertheless, the ratio I_p/W_l for different hν-values was nearly constant as can be deduced from the linear dependence of PAFE-current on laser pulse energy (see Fig. 2(b)). Furthermore, the CMP-technique is not sensitive to absorption processes related to surface states,[29] which seems to be important in the case of light absorption in diamond needles. A good qualitative agreement of the R-hν dependence was found with CMP spectra of undoped CVD diamond films with a thickness of about 50 μm containing rather a low nitrogen concentration of ca. 10 ppm.[30,31] Thinner CVD layers of about 1 μm used, e.g., in UV-detectors exhibit a slightly different trend for $h\nu < 5.26$ eV,[32] with photoresponsivity values similar to those observed in our experiments.

According to the data available from optical studies of CVD diamond films, the penetration depth for photons of 5.9 eV at the base of the diamond needle does not exceed 5 μm,[31] which limits free carrier generation only to this region at the base of the needle. Thus, the interpretation of the observed PAFE has to include a transport mechanism of free carriers from the base of the needle to the emission point at the apex which is more than 100 μm away. Excitons, i.e., bound states of electrons and holes introduced by Frenkel,[33] are well known to exist in diamond and are located at 0.2–0.3 eV below the bottom of the conduction band.[34,35] They may propagate over a large distance in the lattice as a traveling wave packet transporting energy. The measured excitation spectrum at a constant voltage (Fig. 3(a)) has a threshold at the exciton energy level, and thus the presence of the excitonic states can explain the observed behavior. In particular, for a two-dimensional expansion of excitons in high-purity CVD diamond, a diffusion length of at least 34 μm at 300 K was reported.[36] Within this diffusion length, excitons may recombine. However, in our case, an electric field is created in diamond, and thus, an efficient conversion of excitons to free carriers, i.e., their ionization, is expected.[37–39] Moreover, the induced free carriers may also be accelerated and propagate through the diamond crystal over the distances up to 30 μm in the presence of electric fields, the so-called "hot electrons."[40–43] Finally, a significant amount of the "hot electrons" generated in the bulk may reach the emission point and contribute to the overall photostimulated increase in the FE-current.

As shown in Fig. 3(b), photoresponsivity increases rapidly with a voltage increase and saturates at about $R = 47$ mA/W for voltage values above 600 V. This dependence can be also explained by the field assisted exciton ionization. Ramping up the voltage causes the increase in the exciton ionization probability and the corresponding increase in the current. At a certain voltage, all excitons generated by the laser irradiation are ionized and current saturation is observed. Furthermore, higher current in the saturation region could be achieved only by increasing the laser pulse intensity.

In conclusion, the field emission characteristics and the photo response of a single diamond emitter were investigated under pulsed laser illumination from the back side. The emitter revealed a significant photo response up to 47 mA/W for a photon energy of 5.9 eV at an applied electric field of 3.5 MV/m. The measured spectral dependency corresponds to the density of states of CVD diamond with excitonic levels in the band gap, which can be excited by photons with energy above 5.2 eV. The origin of the photoconductivity was suggested to be most likely due to the ionization of the excitons in the bulk and subsequent transport of generated "hot electrons" to the emission point, which explains the observed linear dependence of PAFE-current on laser power and its saturation with the applied voltage increase.

See supplementary materials for further experimental details.

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