Capacitive effect in ultrafast laser-induced emission from low conductance diamond nanotips

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Keywords: diamond nanotips, field emission, femtosecond photoemission

Abstract

Single crystal diamond nanotips reveal a new behavior for ultrafast laser-induced electron emission. Under tightly focused femtosecond laser illumination, electron yield shows a saturation with the laser intensity. When the DC bias is sufficient for dark field emission, large optical intensities can switch off the emission occurring between laser pulses during a few hundred μs, because of the low conductance of the diamond tip. We propose a macroscopic model to combine a capacitive effect with the different conduction and emission mechanisms. This study shows that non-metallic photocathodes offer different perspectives from the conventional metallic ones.

1. Introduction

Nanotip-based laser-induced electron emission [1, 2] can produce ultra-short electron wavepackets with high brightness. These sources surpass the performances of photocathodes because of the small effective source size and provide high DC and optical field enhancements. Over the last decade, they have allowed the development of ultrafast transmission electron microscopes [3–6], as well as new types of fundamental investigations of quantum systems, such as strong-field and attosecond physics [7–12] and laser-induced manipulation of quantum systems [13, 14]. So far, most studies are using nanotips from metallic materials since they can provide high currents and their fabrication process is well-controlled. Recently, diamond has become an alternative to metallic materials because of its excellent material properties (mechanical robustness, chemical inertness) and the possibility of a negative electron affinity associated with hydrogen termination [15–17]. Single-crystal diamond nanotips [18] welded on tungsten tips have been used as continuous point electron sources [19]. The electron emitters constituted by single crystal diamond needles, or nano-diamond-coated tips [20] have demonstrated excellent mechanical stability and robustness under laser illumination and strong electric current. In the case of single crystal nano-needles with high electrical conductivity, the photo-excitation remains the dominant cause of electron emission at both low and high repetition rate of the laser, due to the high thermal conductivity of the diamond [21, 22].

It was demonstrated in [19, 23] that diamond nanotips can act as a point electron source. Using a bias voltage $V_{\text{DC}}$ of a few hundreds of volts, currents in the range of the nA can be obtained. This emission is associated with Poole–Frenkel (PF) conduction [24] along the dielectric part of the diamond nanotip, which translates into a voltage drop $\Delta V$ between the base and the apex of the nanotip. In [23], we showed that the PF conduction can be associated to Fowler–Nordheim (FN) tunneling at the apex, both mechanisms contributing to the current with macroscopic conductance of the same order of magnitude. In the following, we show that these nanotips present a new unexpected behavior under femtosecond laser illumination (300 fs pulse duration at a wavelength of 1030 nm). We interpret the emission with a macroscopic model, which can predict experimental data very well.
2. Experimental setup

The diamond nanotip we use are the same as the ones used for the investigation of DC-field emission in [23] and the experimental setup is similar (figure 1(a)). The single crystal diamond nanotips are biased with a voltage $V_{\text{DC}}$ and their apex is illuminated by tightly focused ($\approx 3\, \mu\text{m}$ focal size) near-IR femtosecond laser pulses at 1030 nm, with a 300 fs pulse duration and a variable repetition rate between 1 kHz and 2 MHz. The total emitted current is measured via a picoammeter. An MCP-based retarding field spectrometer measures the kinetic energy of the emitted electrons in the counting regime, as well as the spatial profile of the emission in a field emission microscopy (FEM) configuration. DC field emission can be observed for tip bias above 250 V with the spectrometer, and above 500 V with the picoammeter (limited by the resolution of approximately 50 pA). Laser-induced FEM on similar samples has been studied in [25] but with a large laser focus, so that the whole diamond nanotip was illuminated and not just its apex. In this configuration, laser illumination mostly modifies the conduction properties inside the diamond sample. Here we focus on the effect of laser illumination on field emission at the apex, with the assumption that the conduction mechanisms remain unaffected.

3. Results

In these conditions, we observed that femtosecond laser-induced emission from diamond nanotips exhibits several features that are very different from metallic nanotips, especially in the case where the bias $V_{\text{DC}}$ on the tungsten tip supporting the diamond needle is high enough so that we observe electron emission without laser illumination. We focus on this regime in the following. We present the dependance of the total emitted current $I$ on laser intensity or pulse energy $E$ in figure 1(b) for a tip bias $V_{\text{DC}} = 500\, \text{V}$ and a repetition rate of 1 MHz. It shows that the total emitted current has a step-like behavior with three distinct regimes: for low intensities [regime (I)], the 50 pA current equals the one of static emission without laser illumination. For higher pulse energies, the current quickly rises [regime (II)], and after a certain value, the current saturates at approximately 350 pA [regime (III)]. This increase in current is associated with a modification of the field-emission pattern, which we measured with FEM map shown in figure 1(b). While the DC emission appears as a single emission spot, with increasing laser pulse energy the FEM pattern becomes a large ring with decreasing diameter, up to a large emission area of a few mm². We associate this effect to an electrostatic lens due to a charge deficit at the apex of the diamond tip. This charge deficit will be discussed below, but the investigation of the ring pattern shape would require a microscopic model for the current and is outside the scope of this article.

Since the quick rise of the current with the pulse energy is non-linear, we assume it is because of multiphoton absorption. We try to identify the multiphoton order by plotting the current vs pulse energy in logarithmic scale $\ln(I - I_0)$ vs $\ln(E)$, where the DC field emission current $I_0 = 53\, \text{pA}$ is subtracted from the total current figure 1(c). We found a nonlinear exponent of 4.2, indicating the absorption of more than 4 photons before an electron is emitted. This is coherent with other studies of photoemission from diamond-based nanotips [21, 22], where photoemission was observed from different channels including...
Figure 2. Gated measurements of electron emission currents and corresponding FEM maps for 200 nJ laser pulses and $V_{\text{DC}} = 600$ V. The displayed current corresponds to the average value, without taking the efficiency of the MCP-based detection into account (which is on the order of 2%) but with a spatial integration over the whole measurable emission map [in (a) and (b) only]. (a) At high repetition rates (here 10 kHz), photoemission cancels the DC current between laser pulses. (b) At lower repetition rates (here 1 kHz) the DC current appears in between pulses, with a different FEM pattern. (c) Dynamics of the current between laser pulses at 1 kHz. Current is displayed as a function of the delay $\tau$ between the laser pulses and a 50 $\mu$s gate. In this case the current is detected through a pinhole, which explains why the value is lower than in (a) and (b).

Additionally, we measured the kinetic energy $E_{\text{kin}}$ of the emitted electrons using the retarding-field spectrometer in the counting regime, and we found that the emitted electrons have a kinetic energy $E_{\text{kin}} = eV_{\text{apex}} < eV_{\text{DC}}$ with $V_{\text{apex}}$ being the electrostatic potential at the apex. The voltage drop along the diamond nanotip is denoted $\Delta V$. Results are shown in figure 1(d) for different laser pulse energies at a repetition rate of 500 kHz. Without laser illumination, we observed an affine dependence of $V_{\text{apex}}$ on $V_{\text{DC}}$ with a slope of 0.47 and an intercept of approximately 100 V [23]. For low pulse energies [regime (I)], the apex potential is identical to that of DC emission. In the saturation regime (III), it shifts down while keeping a similar slope so that it is now linear with a slope of $\alpha = 0.49 \pm 0.01$. Our experimental setup could not allow us to measure precisely the apex potential in the intermediate regime (II) where the current quickly rises because in this regime, the spatial distribution of photoelectrons was too broad [see FEM maps in the regime (II) in figure 1(b)].

Another unique feature of the photoemission process from these single crystal diamond nanotips is their ability to cancel DC field emission in the saturating regime. We used a gated detection setup for the spectrometer to observe this effect, and it works as follows: two complementary gates are used, generated by a digital delay generator (SRS DG535), triggered by the femtosecond laser source. Gate G1 is located around the laser pulses, with a duration of 200 ns. Gate G2 is complementary to gate G1 so that it allows measurements in between laser pulses. The long duration of gate G1 was necessary because of electrical rebounds in the detection signal, and so that adding the currents from gates G1 and G2 gives the total emitted current. Results are shown in figures 2(a) and (b) for a tip bias $V_{\text{DC}} = 500$ V and two different repetition rates with 200 nJ laser pulses. Using a large laser repetition rate (10 kHz and higher), we observed no current during gate G2 when high energy laser pulses are illuminating the tip. In this case, all emitted electrons are detected during gate G1. However, for low repetition rates, i.e. for long duration between laser pulses, we observed that the DC emission can appear in between pulses, which we can identify clearly because of its different spatial profile. We interpret this phenomenon as a capacitive effect at the tip apex: if the tip bias is large enough to have an observable field emission current, the photoemission induced by high laser pulse energies will drain all existing charges at the apex so that the apex field is not high enough for
DC emission to recover in between laser pulses. A specific model is discussed below to account for these observations.

The temporal dynamics have been studied in a subsequent experiment depicted in figure 2(c). A delayed detection gate of 50 μs duration is used, and the delay τ after the laser pulse is translated, so that we can record the emitted current during that gate as a function of τ. Results for various tip biases between 450 and 600 V are shown in figure 3. As expected from the previous observation, the current increases over a characteristic time of several hundreds of μs (hence the difference between 1 and 10 kHz in the previous measurement). The current increase is similar to a first order behavior (like the charge of a capacitor), except that the rise time here depends on the applied voltage, 200 μs at 600 V and over 1 ms at 450 V.

4. Capacitive interpretation of the temporal dynamics

In the following we introduce a macroscopic model to account for all these observations (a more detailed description of the assumptions and calculations are available in the appendix A). It extends and completes the model introduced in [23] for DC emission with a slight modification. In that case, we modeled the system as the combination in series of PF conduction in the diamond tip with FN tunneling at the apex. Here, we start by simplifying the charge distribution inside the diamond nanotip, and divide the carriers into two parts: the total charge of the carriers located at the apex that will contribute to the photoemission is noted $Q_{PE}$ and the rest of the charge (background carriers) is noted $Q_{back}$. Both contributions will contribute to the potential $V_{apex}$ and field $F_{apex}$ at the apex, so that we can write

$$ V_{apex} = V_{PE} + V_{back} $$

$$ F_{apex} = F_{PE} + F_{back} = \beta_{PE} V_{PE} + \beta_{back} V_{back} $$

where $V_{PE}$ and $F_{PE}$ (respectively $V_{back}$ and $F_{back}$) are the potential and field created at the apex by $Q_{PE}$ (respectively $Q_{back}$) and $\beta_{PE}$ and $\beta_{back}$ are constants, similar to field enhancement factors.

We assume that the current saturation observed experimentally for high pulse energies corresponds to the case $Q_{PE} \rightarrow 0$, so that the linear dependence of the apex potential with the tip bias translates into $V_{back} = \alpha V_{DC}$ (see appendix A for more details). We suppose that this relation always holds, also in the case where laser illumination does not saturate electron emission. We can therefore write:

$$ F_{apex} = \beta_{PE}(V_{PE} + \delta V_{DC}) $$

with $\delta = \frac{\alpha}{\beta_{PE}}$ a constant dimensionless parameter. This field at the apex is responsible for FN emission, and the FN current $I_{FN}$ depends on the apex field $F_{apex}$ as well as the material properties of the nanotip.

$$ I_{FN} = C' F_{apex}^2 \exp \left( - \frac{D'}{F_{apex}} \right) $$

$$ = CV_{FN}^2 \exp \left( - \frac{D}{V_{FN}} \right) $$
where \( C', D', C = C'\beta_{PE}^2 \) and \( D' = D/\beta_{PE} \) are constants and with

\[
V_{FN} = V_{PE} + \delta V_{ape} = F_{ape}/\beta_{PE}.
\]

This artificial potential \( V_{FN} \) is used rather than the field apex because FN currents are usually computed with voltages rather than fields, and so that we do not need to explicitly compute the field enhancement factors \( \beta_{PE} \) and \( \beta_{back} \). The constants \( \delta, C \) and \( D \) can be estimated using the DC measurements of the current and apex potential (see appendix A). We find \( \delta = 0.2, C = 1.6 \times 10^{-12} \text{ A V}^{-2} \) and \( D = 1.61 \times 10^3 \text{ V} \). Similarly, the PF current can be written as

\[
I_{PF} = A \Delta V \exp \left( B\sqrt{\Delta V} \right)
\]

with \( \Delta V = V_{DC} - V_{ape} \) and the constants \( A \) and \( B \) being evaluated using the DC measurements (see appendix A and [23]). We take \( A = 3.1 \pm 0.05 \times 10^{-14} \text{ A V}^{-1} \) and \( B = 0.239 \pm 0.001\sqrt{\text{V}} \).

The evolution of the photoemission charge at the apex \( Q_{PE} \) can be computed during the time between laser pulses. It must obey the conservation of charge. If we assume that this charge is feeded by the PF current \( I_{PF} \), and is leaking because of the FN current, we can write

\[
\frac{dQ_{PE}}{dt} = I_{PF} - I_{FN}.
\]

Both \( I_{PF} \) and \( I_{FN} \) can be expressed as a function of \( V_{PE}, V_{DC}, \alpha \) and \( \delta \). We can additionally relate the proportionality between the charge \( Q_{PE} \) and the potential \( V_{PE} \) it creates at the apex as \( Q_{PE} = KV_{PE} \) with \( K \) an effective capacitance for the tip apex. We then find the following nonlinear differential equation for \( V_{PE} \):

\[
K \frac{dV_{PE}}{dt} = A\Delta V \exp \left( B\sqrt{\Delta V} \right) - CV_{FN}^2 \exp \left( -\frac{D}{V_{FN}} \right)
\]

where \( \Delta V \) and \( V_{FN} \) can be expressed as functions of \( V_{PE}, V_{DC}, \alpha \) and \( \delta \). In order to estimate the initial value after the laser pulse \( V_{PE}(t = 0^+) \), we make the following assumption: at \( t = 0^- \), just before the ultrashort laser pulse, each electron composing \( Q_{PE} \) has the same probability \( p_0 \) to be photoemitted. This means we can write

\[
Q_{PE}(t = 0^+) = (1 - p_0)Q_{PE}(t = 0^-)
\]

with \( p_0Q_{PE}(t = 0^-) \) being the charge emitted by a single laser pulse. \( p_0 \) then depends on the laser pulse characteristics (pulse energy, duration and focus size). Equation (10) also holds for \( V_{PE} \). For low laser repetition rates, \( V_{PE}(t = 0^-) \) is equal to its DC value because the duration between laser pulses is long enough for the DC current to recover as discussed above (see appendix B).

For each solution of equation (9), we can calculate the corresponding FN current versus time using equation (5). We used this method to fit the experimental data of figure 2(c) for \( V_{DC} = 600 \text{ V} \) in order to retrieve numerical values for \( K \) and \( p_0 \). We find \( K = 4.5 \times 10^{-16} \text{ F} \) and \( p_0 = 0.85 \). Additional solutions for different values of \( V_{DC} \) are calculated with no extra fitting parameters, and compared to experimental data. Results are shown in figure 3. This works well for \( V_{DC} = 550 \text{ V} \). For lower values of \( V_{DC} \), we had to adjust the numerical value of \( p_0 \) to account for the fact that the 1 ms between laser pulses was not enough for \( V_{PE} \) to get to its DC value. However, the photoemission probability should not depend on the applied voltage and only depend on the laser pulse characteristics, as discussed below.

For \( p_0 = 0.85 \), starting from a DC value for \( Q_{PE} \) and \( V_{PE} \), the first laser pulse triggers the emission of 85% of the available electrons. Of course, this value depends on the laser pulse peak intensity and duration (and therefore pulse energy), as well as the photoemission mechanism. In appendix B, we interpret qualitatively the numerical values of capacitance and charges that can be retrieved from the fitted values for \( K \) and \( p_0 \).

5. Model for the current saturation under large intensities

We now have all the ingredients to compute the expected current for any laser power and repetition rate within our model. For repetition rates higher than \( 1/\tau \), the local charge \( Q_{PE} \) does not have enough time to reach its stationary value, so that the local charge after a second pulse is smaller than after the first pulse, and so on and so forth. After several laser pulses, \( Q_{PE} \) reaches a value close to zero so that the local charge \( Q_{PE} \) never reaches a value sufficient for FN field emission and only photoemission is observable. This corresponds to what has been observed experimentally in the saturation regime discussed above. For different laser pulse energies, the photoemission probability \( p_0 \) that we estimated before needs to be replaced by a function \( p(E) \) of the pulse energy. If we assume that the photoemission is multiphotonic of
order $n$, we can assume a power law for $p(E)$ in the form

$$p(E) = p_0 \left( \frac{E}{E_0} \right)^n = \left( \frac{E}{E_1} \right)^n \quad \text{for} \quad E \leq E_1 \quad (11)$$

where $E_0$ is the pulse energy corresponding to $p_0$ and $E_1$ is the pulse energy for which $p = 1$. If $E > E_1$ we assume that $p = 1$, i.e. all available charges for photoemission are emitted during the laser pulse, and the photoemission current cannot grow larger. This is obviously a limitation of our model, which does not account for the spatial distribution of the photoemission charge. We think however that it is enough to explain all the experimental observations, such as the three regimes observed for the emitted current in figure 1(b).

The total current emitted from the diamond nanotip is the sum of the photoemission current ($pQ_{PE} \times$ repetition rate) and the FN current between laser pulses. If the repetition rate is large enough, only the photoemission current is relevant. We calculated the total current versus pulse energies for different values of the tip bias $V_{DC}$ and compared them with experimental data. Results are shown in figure 4. No extra fitting parameters were necessary, but the energy $E_1$ had to be slightly tuned to account for laser misalignments for each measurement. We find that with $n = 4$, we have good agreement with the experiments, which shows that our model is relevant to describe and predict the behavior of laser-induced electron emission from diamond nanotips. The influence of the laser repetition rate on the current saturation is discussed in appendix C.

6. Conclusion

We have shown that single-crystal diamond nanotips can act as ultrafast photocathodes in addition to their DC field emission properties. Their photoemission properties allow moderate currents in the nA range with tip bias of a few hundred volts. Under intense femtosecond laser illumination, the current saturates because of a capacitive effect associated with low conductivity of diamond: the low conductance inside of the diamond tip delays the charge accumulation at the apex. Although this effect can be undesirable when high currents are needed, it can also prevent current fluctuations due to the misalignment of the laser focus over time. We also demonstrated that in this saturation regime, photoemission cancels the DC emission over a few hundreds of $\mu$s, acting as an ultrafast off-switch for field emission. We introduced a macroscopic model that can accounts for all our observations, based on the separation of the carriers in diamond. This model could be used in other types of non-metallic photoemitters where the current is limited by the conduction and not the tunneling, as well as other types of laser illumination.

Acknowledgments

The authors thank Alexander Obraztsov for providing the diamond needles. This work was supported by Program Investissements d’Avenir under the Programs ANR-11-IDEX-0002-02, reference ANR-10-LABX-0037-NEXT, ANR-13-BS04-0007-01 and ANR-10-LABX-09-01, LabEx EMC3, by the European Union with the European Regional Development Fund (ERDF) and the Regional Council of Normandie.
Appendix A. Determination of the electrostatic constants from DC field emission measurements

The model we present to explain the experimental observations of the photoemission from diamond nanotips is a macroscopic model. It aims at simplifying the charge distribution in the diamond by separating two contributions, each of them contributing to the potential and field at the nanotip apex as shown schematically in figure 5. The charges at the apex, denoted \( Q_{\text{PE}} \), are the charges available for photoemission and the rest of the charge, which we call background charges, are denoted \( Q_{\text{back}} \). We make the assumption that the exact distribution of charges is not relevant here so it could be surface or volume charges. The photoemission charges \( Q_{\text{PE}} \) are of course also available for FN tunneling, but since the FN formalism only depends on the field at the apex, it is not straightforward that the charges \( Q_{\text{PE}} \) also dictates directly the FN current. Looking at the timescales, the photoemission charges are released over a fraction of a picosecond, whereas for FN, the typical currents we observe in the nA range correspond approximately to one electron every 100 ps. Charges could very well be redistributed during that time, and we chose to keep the standard calculation of the FN current, depending only on the field at the apex.

As stated in the article, we have:

\[
V_{\text{apex}} = V_{\text{PE}} + V_{\text{back}} \quad \text{(A1)}
\]

\[
F_{\text{apex}} = F_{\text{PE}} + F_{\text{back}} = \beta_{\text{PE}} V_{\text{PE}} + \beta_{\text{back}} V_{\text{back}} \quad \text{(A2)}
\]

\[
V_{\text{apex}} \] is measured experimentally using the electrons kinetic energy and we have \( V_{\text{apex}} = V_{\text{DC}} - \Delta V \), with \( \Delta V \) the voltage drop along the diamond tip. The saturation of the current in the case of photoemission for large pulse energy corresponds to the case where the photoemission charge \( Q_{\text{PE}} \) must be zero after the laser pulse. Therefore, in this regime, we can assume \( V_{\text{apex}} = V_{\text{back}} \). From the linear behavior of \( V_{\text{apex}} \) with the tip bias, we can infer \( V_{\text{back}} = \alpha V_{\text{DC}} \) with \( \alpha = 0.49 \). We suppose that this relation always holds true, also in the case where laser illumination does not saturate electron emission. This implies that, except for the carriers located near the apex, the charge distribution in the diamond is linear with respect to the apex voltage. We can therefore write:

\[
V_{\text{apex}} = V_{\text{PE}} + \alpha V_{\text{DC}} \quad \text{(A3)}
\]

\[
F_{\text{apex}} = F_{\text{PE}} + F_{\text{back}} = \beta_{\text{PE}} V_{\text{PE}} + \beta_{\text{back}} \alpha V_{\text{DC}} = \beta_{\text{PE}} (V_{\text{PE}} + \delta V_{\text{DC}}) \quad \text{(A4)}
\]

where we identify \( V_{\text{FN}} = V_{\text{PE}} + \delta V_{\text{DC}} \) and use it as an effective potential at the field apex to compute the FN current. \( V_{\text{FN}} \) is not real in the sense that it does not represent the value of the electric potential at a given point, but is rather another way of expressing the field at the apex.

As we described in [23], the DC emission from diamond nanotips combines PF conduction [24] and FN in series, so that the total emitted current can be written as

\[
I = A \Delta V \exp \left( B \sqrt{\Delta V} \right) = CV_{\text{FN}}^2 \exp \left( - \frac{D}{V_{\text{FN}}} \right). \quad \text{(A6)}
\]

Using PF coordinates (\( \ln(I/\Delta V) \) versus \( \sqrt{\Delta V} \)) to plot the current, we can estimate the parameters \( A \) and \( B \), and we find \( A = 3.1 \pm 0.05 \times 10^{-18} \, \text{A}^{-1} \) and \( B = 0.239 \pm 0.001 \sqrt{V} \) [23]. To identify the FN coefficients \( C \) and \( D \) as well as the parameter \( \delta \) is not straightforward. Because \( \delta \) is unknown, we cannot use directly FN coordinates \( \ln(I/V_{\text{FN}}^2) \) versus \( 1/V_{\text{FN}} \). Instead, we fitted both the current \( I \) and the apex potential \( V_{\text{apex}} \) with respect to \( V_{\text{DC}} \). With 3 fitting coefficients, fitting is less restrictive and results were convincing for \( \delta \) between 0.2 and 0.28 with different values of \( C \) and \( D \) (figure 6(a)). We chose \( \delta = 0.2 \) which value gave more satisfying results for the temporal studies performed after. For this value of \( \delta \), we have

![Figure 5. Separation of the electric charge in diamond used in our model. The apex potential and field will have contributions from both the apex charges \( Q_{\text{PE}} \) available for photoemission, as well as the background charge \( Q_{\text{back}} \).](image-url)
Figure 6. Top: measured current (triangles) and fit result (line) for the current plotted in the new FN coordinates \( \ln(I/V_{FN}^2) \) versus \( 1/V_{FN} \). Bottom: for comparison, the same was done using conventional FN coordinates \( \ln(I/V_{DC}^2) \) as a function of \( 1/V_{DC} \). In these coordinates, the agreement is less satisfying and the data points are less linear.

Figure 7. Colored lines: calculated values for the various potentials relevant for the description of the DC conduction and emission mechanisms in the diamond nanotips. Green triangles: experimental data points for the apex potential, measured from the kinetic energy of emitted electrons in DC emission.

\[
C = 1.6 \pm 0.1 \times 10^{-12} \text{ A V}^{-2} \text{ and } D = 1610 \pm 10 \text{ V.} \]  
For these values, the agreement with experimental data is better than when using the apex voltage instead of \( V_{FN} \) (figure 6(b)) as in [23].

Figure 7 shows the calculated values of the different potentials versus the tip bias in DC field emission, as well as the experimental data for the apex potential. In our experimental range for \( V_{DC}, V_{apex}, V_{FN} \) and \( V_{back} \) are close to linear, but the potential \( V_{PE} \) created by the apex charge \( Q_{PE} \) is almost constant.

The numerical values of the fitting parameters \( \alpha, \delta, A, B, C \) and \( D \) that we retrieved could be interpreted in a physical sense, and linked to the characteristics of the diamond nanotip itself (workfunction, temperature, radius, mobility, \ldots). However, since a lot of them are unknown, we choose not to discuss or calculate these physical parameters from the fitting parameters.
This macroscopic model differs from the more simple one developed in [23] in the sense that we do not consider the apex field to be linear with respect to the apex potential, which means the field enhancement factor $\beta_{\text{apex}} = F_{\text{apex}} / V_{\text{apex}}$ is no longer supposed to be constant. Here, we made the less strong assumption to take the relative enhancement factors $\beta_{\text{PE}}$ and $\beta_{\text{back}}$ to be constant. From the numerical values of $\alpha$ and $\delta$, we can calculate the relative variation of $\beta_{\text{apex}}$ with respect to $\beta_{\text{PE}}$ as

$$\frac{\beta_{\text{apex}}}{\beta_{\text{PE}}} = \frac{V_{\text{PE}}}{V_{\text{DC}}} + \delta \frac{V_{\text{PE}}}{V_{\text{DC}}} + \alpha.$$  

(A7)

Results are shown in figure 8 where this quantity is plotted versus the tip bias $V_{\text{DC}}$. In this model, we have thus a field enhancement factor that scales down with respect to the tip bias, with a decrease of approximately 20% over the range of the tip bias we use in our experiment. This is rather small, and explains why our more simplistic model [23] with a constant field enhancement factor was sufficient to account for the DC observations.

### Appendix B. Temporal evolutions of charges and potentials

As we described in the article, introducing an effective capacitance $K$ for the photoemission charge $Q_{\text{PE}}$ allows us to write the evolution equation of the potential $V_{\text{PE}}$ in the following form:

$$K \frac{dV_{\text{PE}}}{dt} = A \left[ (1 - \alpha) V_{\text{DC}} - V_{\text{PE}} \right] \exp \left( B \sqrt{(1 - \alpha) V_{\text{DC}} - V_{\text{PE}}} \right) - C [V_{\text{PE}} + \delta V_{\text{DC}}]^2 \exp \left( - \frac{D}{V_{\text{PE}} + \delta V_{\text{DC}}} \right).$$  

(B1)

The initial condition of this equation is described using the photoemission probability $p_0$ of each electron:

$$V_{\text{PE}}(t = 0^+) = (1 - p_0)V_{\text{PE}}(t = 0^-)$$  

(B2)

where we consider the photoemission to be instantaneous at $t = 0$. This is justified by the very short duration of laser pulses (300 fs) compared to the characteristic time observed for the establishment of DC emission between laser pulses (several hundreds of $\mu$s). Equation (B2) assumes that the photoemission probability is identical for all electrons within $Q_{\text{PE}}$. This means that in our macroscopic model, we neglect the spatial distribution of the electrons at the apex. In reality, the non-uniform distribution of the laser field at the apex would result in different photoemission probabilities for each electron.

For low repetition rates $V_{\text{PE}}(t = 0^-)$ can be identified to $V_{\text{PE}}(t = \infty)$ which corresponds to DC values. In our experiment, the temporal dynamics of the FN current $I_{\text{FN}}$ between laser pulses was measured for single electrons using gating on the micro-channel plate based spectrometer. The picoammeter could measure the PF current $I_{\text{PF}}$ (different to $I_{\text{FN}}$ in this case), but it is not able to give precise measurements over such short times. Since the spectrometer has a limited detection efficiency, we normalized the measured current by assuming that we reach the DC value of the current for long times.
Figure 9. Effect of the laser repetition rate on the current saturation with the pulse energy. Triangles correspond to experimental data and the line to the numerical model.

For each values of $K$ and $p_0$, we can solve numerically equation (B1) and compute $I_{FN}(t)$. As stated in the article, we used this method to fit the experimental data, and retrieve the following numerical values:

$$K = 4.5 \times 10^{-19} \text{F} \text{ and } p_0 = 0.85.$$  

The capacitance $K$ of the tip, associated to the value of the FN resistance $R_{FN} = V_{FN}/I_{FN} = 2.53 \times 10^{12} \Omega$ (calculated for $V_{DC} = 600 \text{ V}$ and $V_{FN} = 292 \text{ V}$) gives us a timescale $\tau = K R_{FN} = 600 \mu\text{s}$. This corresponds only approximately to the rise time of the FN current measured experimentally since we used the DC value for $V_{FN}$ to calculate $\tau$. The FN resistance actually varies during the charge. It also depends on the tip bias, which explains why it takes longer to reach the DC emission for lower tip bias. The numerical value of $K$ can also be interpreted as follows: the electrons contributing to $Q_{PE}$ have an unknown spatial distribution, and the potential $V_{PE}$ can be written as

$$V_{PE} = \sum_i \frac{e}{4\pi \varepsilon_0 \varepsilon_r r_i} = \frac{Q_{PE}}{4\pi \varepsilon_0 \varepsilon_r \bar{r}}$$  \hspace{1cm} (B3)

with $\varepsilon_r = 5.7$ the relative permittivity of diamond \cite{19}, $r_i$ the distance of charge $i$ to the apex, and $\bar{r}$ the harmonic mean value of $r_i$. We therefore can identify $K = 4\pi \varepsilon_0 \varepsilon_r \bar{r}$, from which we can evaluate $\bar{r} \approx 700 \text{ nm}$. The order of magnitude of $\bar{r}$ corresponds approximately to the focus size of the laser beam, if we take into account that the fourth order non-linearity reduces the effective focus size.

We can also calculate numerically the photoemission charge $Q_{PE}$ at the apex from the value of $K$. For $t \to \infty$ (corresponding to the DC emission case), we find $Q_{PE} = 5.8 \times 10^{-14} \text{ C}$ for $V_{DC} = 600 \text{ V}$, which corresponds to $3.6 \times 10^7$ electrons. With $p_0 = 0.85$, 85% of the available electrons at the apex are emitted at $t = 0$. This process repeats itself after each laser pulse. If the repetition rate is large enough, when the following laser pulses illuminate the tip, the charge will not have reached its static value, the local charge will quickly drop to zero, and the photoemission current will saturate to a maximum. The 350 pA current we measured in the saturation regime (corresponding to $p = 1$) at a repetition rate 500 kHz corresponds to 4000 electrons per laser pulse, which means that within the 2 $\mu\text{s}$ between laser pulses, the local charge has been charged up to only 1% of its DC value.

Appendix C. Influence of the laser repetition rate on the current saturation

The effect of the laser repetition rate can also be implemented in our model and compared to the experimental data. We compared results for measurements at 1 MHz and 250 kHz using the fitting parameters retrieved at 500 kHz. The overall trend agrees well, so that the saturation regime is reached for lower (respectively higher) pulse energies at a higher (respectively lower) repetition rate (figure 9). However, numerical calculations are not as close to the experimental data probably because of the assumptions of our model, that take into account no spatial distribution of the field or the carriers in the apex region.

Appendix D. Interpretation in terms of conductance

From all the results we presented, we have identified two distinct emission regimes. For low laser intensities, DC emission is dominant and electrons are emitted quasi uniformly over time [regime (I) discussed above].

For higher intensities, we reach a saturation [regime (III) discussed above] for which the DC emission disappeared and all the electrons are emitted during the ultrashort laser pulse. This unique feature is due to a capacitive effect associated with the low conductivity of diamond. We can also use macroscopic electric constants to describe the process: PF conduction and FN emission can be described using conductances $G_{PF} = I_{PF} / \Delta V$ and $G_{FN} = I_{FN} / V_{FN}$ in the order of $10^{-12}$ S. They are the same order of magnitude so that for DC emission they contribute both to define the current for a given tip bias. In the case of metallic nanotips, the conductance of the nanotip is very high (in the order of 1 S or less for a conical tungsten nanotip with typical dimensions) so that the field emission current is only governed by the FN behavior. Photoemission can also be associated to an instantaneous conductance $G_{PE} = I_{PE} / V_{PE} = pK / \Delta t$ with $\Delta t$ the pulse duration. We find $G_{PE}$ in the order of $10^{-3}$ S, and if we take the duration and repetition rate into account, we find a mean photoemission conductance $G_{PE}$ in the order of $10^{-9}$ S for high repetition rates. This photoemission conductance is still much higher than the FN conductance, which explains qualitatively why the photoemission is dominating FN emission in our case. It also means that the same behavior could be observed on other types of non-metallic nanotips as long as we satisfy these conditions for the respective conductance.

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