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# Role of plasma-induced defects in the generation of $1/f$ noise in graphene

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It has already been reported that  $1/f$  noise in graphene can be dominated by fluctuations of the charge carrier mobility. We show here that the increasing damage induced by oxygen plasma on graphene samples results in two trends: at low doses, the magnitude of the  $1/f$  noise increases with the dose; at high doses, it decreases with the dose. This behaviour is interpreted in the framework of  $1/f$  noise generated by carrier mobility fluctuations where the concentration of mobility fluctuation centers and the mean free path of the carriers are competing factors.

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Since the advent of graphene-based devices, several groups studied the effects of plasma treatments, mainly oxygen or argon, in order to lower the contact resistance between graphene and metallic electrodes, by means of controlled damage.<sup>1–6</sup> Plasma exposure from a few seconds to few tens of seconds are generally reported to substantially improve the electric contact quality.

We present a study on the behaviour of  $1/f$  noise in graphene damaged by increasing exposure to oxygen plasma dose. We found that there are two trends: at low doses, the magnitude of the  $1/f$  noise increases with the dose, whereas at high doses the magnitude of the  $1/f$  noise is a decreasing function of the dose. This result is interpreted in the framework of  $1/f$  noise generated by carrier mobility fluctuations where the concentration of mobility fluctuation centers and the mean free path of the carriers are competing factors.

Electrical excess noise is a parameter of interest for the characterization of electronic devices, including recently developed graphene-based sensors.<sup>7–10</sup> In particular,  $1/f$  noise constitutes a fundamental limit to the resolution of resistive<sup>11</sup> and Hall effect sensors,<sup>12,13</sup> and the frequency up-conversion of  $1/f$  noise affects amplitude and phase noise of radio-frequency amplifiers, oscillators and detectors.<sup>11</sup> Graphene sensors having electrical noise as output were also proposed.<sup>14–17</sup> As for other materials, the origin of  $1/f$  noise in graphene is not completely understood and subject of considerable debate (see Ref. 11 for a review).

The correlation of  $1/f$  noise magnitude with the amount and type of defects in graphene remains obscure. Hossain *et al.*<sup>18</sup> reports that the magnitude of  $1/f$  noise decreases with increasing damage caused by electron irradiation. In this work, we repeatedly exposed graphene samples to oxygen plasma. The measured  $1/f$  noise magnitude shows a non-monotonic behaviour versus the increasing plasma dose, which can be correlated

to the type and amount of damage quantified by Raman spectroscopy.

For the preparation of the samples, we used commercial graphene grown by chemical vapor deposition on Cu and then transferred on SiO<sub>2</sub>/Si wafer. The plasma etching process was performed in a low pressure atmosphere of oxygen (during the exposition, the pressure was about 10<sup>−3</sup> mbar) at 10 W RF power and 2.5 SCCM<sup>19</sup> oxygen flow for an exposure time  $t_P = 5$  s at each repetition.<sup>20</sup> With these parameters, it is possible to damage the graphene in a controlled way, avoiding the amorphization of the material due to the substitution of sp<sup>2</sup> bonds with sp<sup>3</sup> ones.<sup>21</sup>

The power spectral density (PSD)  $S_v(f)$  of the voltage fluctuations was measured with a digital correlation spectrum analyzer, already employed in Johnson noise thermometry experiments.<sup>22</sup> The sample was excited with a low-noise DC current  $I$ .<sup>23</sup> The noise voltage across the sample was simultaneously amplified by two AC-coupled, two-stage low-noise amplifiers<sup>24</sup> and digitized by a two-channel analogue-to-digital converter board operating at a sampling frequency of 20 kHz.<sup>25</sup> All samples were recorded for off-line processing. Cross periodograms, which reject amplifiers' noise to a large extent,<sup>26</sup> were computed with the Bartlett's method.<sup>27</sup> The typical measurement involves vectors of 2<sup>17</sup> voltage sample pairs, providing estimates of the voltage noise cross PSD  $S_v(f)$  for  $f \approx k \times 0.153$  Hz, where  $k = 1, \dots, 2^{16}$ . All measurements were performed in a shielded environment at  $T = 296.0(5)$  K.

Fig. 1 reports, as an example, the voltage noise PSDs corresponding to three different stages of the experiment. These PSDs show a combination of two noise components: a white noise component at high frequency; a  $1/f$  component at low frequency, with PSD

$$S_v(f) \approx S_v/f^\alpha, \quad (1)$$

$\alpha$  being a constant close to 1 and  $S_v$  characterizing the voltage noise magnitude. From Fig. 1, the crossover between the two components is at about 100 Hz. The white

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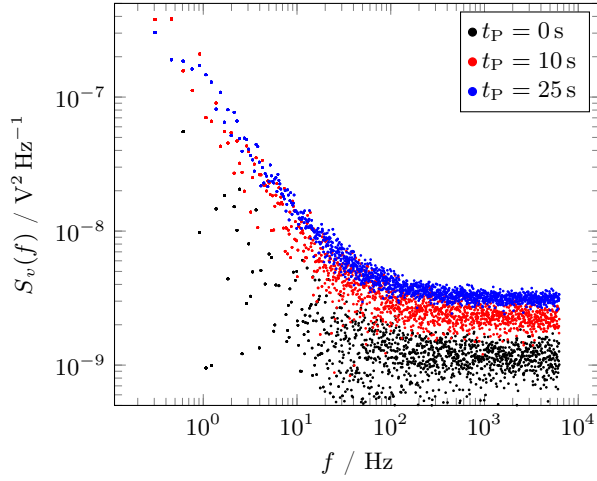


FIG. 1. Voltage noise spectra corresponding to an oxygen plasma exposure time  $t_P$  of 0 s (pristine), 10 s and 25 s.

component of the PSD allows to estimate the sample resistance as  $R = \langle v^2 \rangle / (4k_B T B)$ , where  $\langle v^2 \rangle$  is the noise power over the bandwidth  $B$  and  $k_B$  is the Boltzmann constant. Here we take  $B = 3 \text{ kHz} - 7 \text{ kHz}$ . For the  $1/f$  component, assuming that it is due to resistance fluctuations,<sup>28,29</sup> the relation

$$\frac{S_v(f)}{V^2} = \frac{S_r(f)}{R^2} \quad (2)$$

holds between the PSD  $S_v(f)$ , normalized to the square of the DC voltage  $V$  across the sample, and the PSD  $S_r(f)$  of the resistance fluctuations, normalized to the sample resistance  $R$  squared. Given the relations in Eq. 1 and Eq. 2, we can define the normalized noise magnitude at 1 Hz as:

$$\mathbb{S} = \frac{S_v}{V^2} = \frac{S_r}{R^2}, \quad (3)$$

where  $S_r$  is the resistance noise magnitude and  $\mathbb{S}$  is representative of the material condition at each stage of the experiment;  $\mathbb{S}$  will be used as a first parameter of interest in the following discussion. The level of damage caused by the exposure to oxygen plasma was estimated by means of Macro-Raman spectroscopy, which allows the phenomenological determination of the average distance between the defects. Raman spectra were collected by a tool<sup>30</sup> equipped with a laser source of wavelength  $\lambda_L = 532 \text{ nm}$ , focused onto a spot with a diameter of  $100 \mu\text{m}$ . The relatively wide laser spot allowed to investigate relatively large areas of the sample, averaging over possible pristine structural inhomogeneities of the sample. For the acquisition of each Raman spectrum, the sample was exposed for 60 s to a power density of  $150 \text{ W cm}^{-2}$ .<sup>31</sup> This is important to avoid the formation of unwanted additional laser-induced defects during the characterization.<sup>32</sup> The three Raman spectra shown in Fig. 2 correspond to the three voltage noise spectra shown

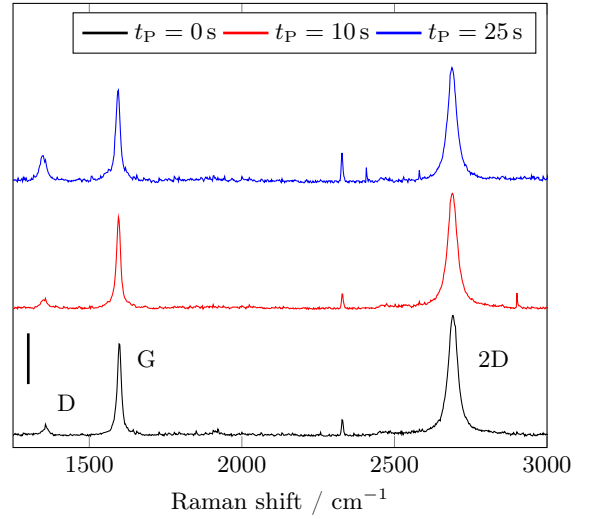


FIG. 2. Evolution of Raman signatures in graphene sample before ( $t_P = 0 \text{ s}$ , pristine) and after 10 s and 25 s of exposure to oxygen plasma. The feature at about  $2300 \text{ cm}^{-1}$  is due to the atmospheric nitrogen along the optical path of the laser beam. The vertical marker at the bottom left represents  $2 \times 10^3$  counts.

in Fig. 1. The peaks D (defective), G (graphitic) and 2D (D overtone) are respectively located at about  $1350 \text{ cm}^{-1}$ ,  $1590 \text{ cm}^{-1}$  and  $2700 \text{ cm}^{-1}$ .<sup>33,34</sup> Fig. 2 shows that exposure to oxygen plasma provokes structural changes in graphene; these can be assessed through the evolution of the above mentioned Raman signatures, in particular the monotonic increase of the D mode and the broadening of the 2D mode. The growth of the D mode indicates the appearance of vacancy- or point-like defects,<sup>35</sup> while the 2D mode broadening gives information about the weak nano-metre scale distortion of the carbon honeycomb lattice.<sup>36</sup> The two phenomena are competitive. The structural changes in the graphene samples due to the appearance of point-like defects can be assessed by the average point-defect distance  $L_D$ , that can be calculated from the Raman spectra following the Tuinstra-Koenig<sup>37,38</sup> relation

$$L_D^2 = (1.8 \times 10^{-9} \text{ nm}^{-2}) \lambda_L^4 \frac{I_G}{I_D}, \quad (4)$$

where the numerical factor in the right hand side of Eq. 4 is empirical,  $\lambda_L$  is the laser wavelength (in nm), and  $I_G/I_D$  is the intensity ratio between the G and the D peaks of the Raman spectrum. This law is considered accurate down to a defect distance of about  $10 \text{ nm}$ .<sup>39</sup> On the other side, the more “gentle” structural change due to weak lattice distortion can be observed following the evolution of the 2D peak full width at half maximum (FWHM). In Fig. 3 can be observed a broadening of the 2D feature within the first damaging cycles.<sup>40</sup>

Note that  $L_D$  is calculated from the  $I_G/I_D$  ratio and the D peak is only sensitive to defects being directly related to the presence of unsaturated bonds.<sup>41</sup> This means

that in case of weak lattice distortion the D peak is less informative about changes in the material. Conversely, the 2D peak broadens prior to the appearance of a strong D signature.<sup>36</sup>

As a third parameter of interest, we consider the mean free path  $l_0$  of a free carrier in our samples. It was calculated from the measured field effect mobility of the graphene. In our samples the mobility is of the order of  $10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for the pristine material and was obtained from back gate field effect measurements, while the carrier concentration  $n$ , of the order of  $3 \times 10^{13} \text{ cm}^{-2}$  was calculated from mobility and resistance measurement. To calculate the mean free carrier path consider the following. The semiclassical approximation for the electrical conductivity  $\sigma_{\text{sc}}$  is (see Ref. 42):

$$\sigma_{\text{sc}} = e^2 \tau \frac{n}{m^*}, \quad (5)$$

where  $e$  is the elementary charge,  $\tau$  is the carrier scattering time,  $n$  is the carrier concentration. The definition of effective mass  $m^*$  to be used in the semiclassical approximation for graphene is (Ref. 43, Sec. II):

$$m^* = \frac{\hbar k_F}{v_F} = \frac{\hbar \sqrt{\pi n}}{v_F}, \quad (6)$$

where  $\hbar k_F$  and  $v_F$  are the Fermi momentum and velocity respectively and  $\mu$  is the carrier mobility. Now since the conductivity can also be written as:

$$\sigma_{\text{sc}} = \mu e n, \quad (7)$$

and

$$l_0 = v_F \tau, \quad (8)$$

the following relation yields the mean free path,

$$l_0 = \frac{\hbar}{e} \mu \sqrt{n\pi}. \quad (9)$$

Fig. 4 reports the three parameters of interest — the resistance noise magnitude at 1 Hz  $\mathbb{S}$ , the average point-defect distance  $L_D$ , and the carrier mean free path  $l_0$  — as a function of exposure time  $t_P$  to the oxygen plasma. The mean free path and defect distance have a monotonic behavior, while  $\mathbb{S}$  initially increases up to a maximum for  $t_P = 10$  s, and then decreases for longer plasma exposure time.

We distinguish between two regimes: in regime  $\mathcal{A}$  at low exposure time,  $t_P < 10$  s,  $l_0$  is decreasing while  $L_D$  is approximately constant, and  $\mathbb{S}$  increases; in regime  $\mathcal{B}$  at high exposure time,  $t_P > 10$  s, the defect distance  $L_D$  becomes comparable to the mean free path  $l_0$ , and  $\mathbb{S}$  decreases. The fact that initially  $l_0$  decreases even though  $L_D$  remains quite constant is not surprising. The carrier mean free path decreases as more defects pile up in the material irrespective of their type. It is then advisable to assume that in the regime  $\mathcal{A}$  the (decreasing)

carrier mean free path is mainly affected by the (increasing) weak nanometre-scale distortion of the lattice rather than by the appearance of point-like defects as occurs in regime  $\mathcal{B}$ .

In a commonly accepted picture for graphene<sup>11,44</sup>, the  $1/f$  noise is due to the fluctuation of the number of charges trapped in the substrate that act as long-range Coulomb scatterers and induces resistance fluctuations in the graphene channel. This seems to be the dominant mechanism in exfoliated graphene at low carrier concentration. Conversely, the CVD growth process yields a material with considerably larger disorder and doping than the exfoliated type. Hence in CVD graphene the short-range scattering becomes more important. Since at large carrier concentration the long-range Coulomb potentials are screened, the role of substrate is less important and the mobility fluctuations are largely due to scattering within the graphene itself.<sup>45</sup>

The following equation adapted from Ref. 46 (originally proposed in Ref. 47) provides a model for systems in which resistance noise is dominated by mobility fluctuations, and where the  $1/f$  noise emerges as a superposition of multiple processes with a wide distribution of characteristic time constants:

$$\frac{S_r(f)}{R^2} = \frac{\mathbb{S}}{f} = \sum_{\tau} \frac{N_{\mu}}{\mathcal{V}} \frac{\tau \zeta(1-\zeta)}{1 + (2\pi f \tau)^2} l_0^2 (\sigma_1 - \sigma_2)^2. \quad (10)$$

In this equation,  $\mathcal{V}$  is the sample volume,  $\tau$  is the characteristic time constant of the elementary process,  $N_{\mu}$  is the concentration of centers that contribute to mobility fluctuations,  $\zeta$  is the probability for a  $N_{\mu}$  center to be in a state with cross-section  $\sigma_1$  (while  $1 - \zeta$  is the probability to be in a state with cross-section  $\sigma_2$ ). Following this model, the resistance noise is proportional to the concentration  $N_{\mu}$  and the mean free path  $l_0$ . In general  $N_{\mu}$  represents metastable lattice centers<sup>48</sup>, like the ones that occur in the first stage of damaging in our samples.

Our findings are in agreement with this model. The quantity  $l_0$  decreases monotonically since it is sensitive to all types of defects. In the regime  $\mathcal{A}$ , the constancy of  $L_D$  and the broadening of the 2D peak suggest that the main type of induced defects is that associated to mobility fluctuations, leading to an increase of  $N_{\mu}$ . The behavior of  $\mathbb{S}$  in regime  $\mathcal{A}$  can be explained in terms of a positive contribution of  $N_{\mu}$ , that countervails the effect of a decreasing  $l_0$ . Conversely, in regime  $\mathcal{B}$  the average point-defect distance  $L_D$  decreases due to the appearance of a different type of defects which do not contribute to  $\mathbb{S}$  anymore, that consequently starts to decrease following  $l_0$ .

The present work indicates that  $1/f$  noise can be ascribed to mobility fluctuations in CVD graphene samples exposed to oxygen plasma treatments. This confirms and extends earlier observations<sup>18</sup> on exfoliated graphene samples damaged by an electron beam. Since a lot of fabrication processes involve plasma treatments, the present results indicate that this practice may increase the  $1/f$  noise in graphene-based devices for short exposure time.

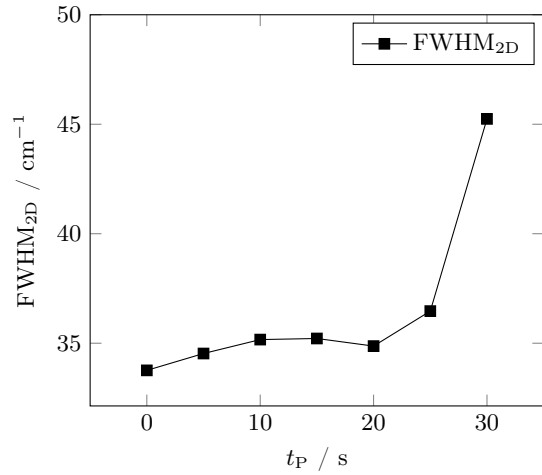


FIG. 3. Full width at half maximum of the 2D peak as a function of the oxygen plasma exposure time  $t_P$ .

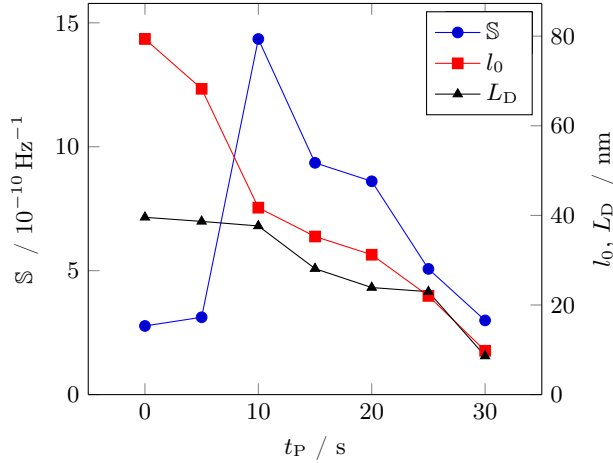


FIG. 4. Resistance noise magnitude at 1 Hz  $S$  (●), carrier mean free path  $l_0$  (■) and average defect distance  $L_D$  (▲), as a function of the oxygen plasma exposure time  $t_P$ .

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