Gas-Selective Signal Amplification in Fluctuation-Based Graphene FET Sensors

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Abstract—The power spectrum of conductance fluctuations arising from the adsorption of gas molecules to a graphene field-effect transistor was shown to contain the signature of the adsorbing species recently. A detailed mechanism of the phenomena was not provided although it was remarked that these conductance fluctuations arise due to the number fluctuations of the adsorbed molecules, which may donate (or accept) electrons to (or from) graphene. In this paper, we report on a phenomenological model based on conductance fluctuations and analyze a novel sensing configuration consisting of a sinusoidally varying gate voltage sweeping across the Dirac point, which changes the sign of conductance response to adsorption. We show that this configuration leads to gas-selective amplification of peaks of the conductance fluctuation spectra.

Index Terms—Conductance fluctuations, power spectrum, gate voltage, sensing configuration.

I. Introduction

GRAPHENE for its excellent mobility, extremely high surface to volume ratio and very good electrical conductivity, is being intensely explored for various applications including gas-sensing [1]–[5]. In these sensors, the adsorption of gas molecules on the graphene surface leads to change in conductance across the graphene. Typically, graphene gas sensors have Field Effect Transistor (Gr-FET) configuration with the possibility of controlling the flow of charge carriers through the graphene layer using a gate electrode. The conductance change during gas adsorption can be positive or negative depending on whether the gas molecule is an electron donor or acceptor as well as depending on the gate voltage applied, i.e. whether the gate voltage is above or below the Dirac point which determines whether the Gr-FET is operating in the electron or hole dominated conduction regime [6]. Gr-FET based gas sensors are known to be operated based on the shift in conductance due to gas adsorption [7], [8]. Recent study shows that, not only the conduction shift but the fluctuation of the conductance can also be used for sensing of gas adsorption on graphene [1], [9]. In these works, it is also shown that not only the conductance fluctuations arising from the adsorption of gas molecules to a Gr-FET contain the gas signature but can also be used for identification of gas species in a mixture of gases. These conductance fluctuations arise due to the number of fluctuations of the adsorbed molecules which may denote (or accept) electrons to (or from) graphene. These number fluctuations result in a deviation from the 1/f dependence of the power spectrum and appear as a broad peak in the product of power spectrum and frequency. The position of this peak was different for the different gas molecules considered which helped in the selective identification of the adsorbing gas species. In this paper we present a quantitative phenomenological model of gas sensing based on conductance fluctuations in a Gr-FET sensor and estimate numerical parameters for the model from the reported experimental observations. We then analyze a novel sensing configuration using Gr-FETs where the gate voltage is sinusoidally swept across the Dirac point. This causes the conductance regime in graphene to alternately switch from electron dominated to hole dominated conduction. This means that an addition of an electron or hole may result in an increase or decrease in the conductance depending on the operating regime resulting in a modification of the statistics of conductance fluctuations and a consequent alteration of its power spectrum. We show that this sensing configuration results in an amplification of the conductance fluctuations, i.e. the selective signal can be enhanced by imposing the external modulation. In the subsequent sections we describe this phenomenon in greater detail.

II. Model for Conduction Fluctuations

We consider a system, where a Gr-FET is exposed to n number of chemical vapors. We assume a) the adsorption-desorption process is stochastic in nature, b) there are no chemical reactions occurring between the gases in mixture and c) the physical properties are restored during the adsorption-desorption process. For species i, stochastic variations in the number of molecules which are adsorbing and desorbing from a surface lead to fluctuations of the number of molecules adsorbed on a surface. The rate of adsorption of component i, at any time t, obeys the rate equation (1).

$$\frac{dN(t)}{dt} = \alpha p (N_0 - N(t)) - \beta N(t) \tag{1}$$

where α and β are the adsorption and desorption rate constants of component i.

From this, it follows that at equilibrium, the fluctuations of $N(t) = N_{eq} + \delta N(t)$, satisfies the equation,

$$\frac{d\delta N(t)}{dt} = -\frac{\delta N(t)}{\tau} \quad (2)$$

Here, $\tau = \frac{1}{\alpha p + \beta}$

Then,

$$\delta N(t) = \delta N_0 e^{-t/\tau} \quad (3)$$

The power spectrum of number fluctuations $S_{\delta N}$ can be written as

$$S_{\delta N} = \delta N_0^2 \left| FT\left(u(t)e^{-t/\tau}\right)\right|^2 \quad (4)$$

Here u(t) is the unit step function inserted to take into account causality. Using the relation

$$FT\left(u(t)e^{-t/\tau}\right) = \frac{\tau}{1 + j\omega\tau} \quad (5)$$

$$f(t) = u(t)e^{-t/\tau} \quad (5a)$$

$$|FT(\{f(t)\}|^2 \omega = F(\omega) \quad (5b)$$

$$S_{\delta N} = \delta N_0^2 \frac{\tau^2}{1 + (\omega\tau)^2} \quad (6)$$

The conductance of the graphene FET for component i can be written as

$$\sigma(t) = \gamma N(t) = \sigma_0 + \gamma_0 \delta N(t) \quad (7)$$

Then the power spectrum of the conductance fluctuations of component i will then be

$$S_\sigma = \gamma_0^2 \delta N_0^2 \frac{\tau^2}{1 + (\omega\tau)^2} \quad (8)$$

The measured power spectrum will consist of the term in Eq. (8) as well as a ubiquitous 1/f noise term. So the combined measured power spectrum for component i can be written in terms of frequency as,

$$S_{meas} = \frac{A}{f} + \frac{B}{f_c^2 + f^2} \quad (9)$$

Where, $B = (\gamma_0 N_0 / 2\pi)^2$

Rumyantsev *et al.* consider the product of the frequency with the power spectrum, defined here as $H = fS$ yielding

$$H_{meas} = A + \frac{Bf}{f_c^2 + f^2} \quad (10)$$

It is easy to see that the quantity H will have a peak at a frequency $f = f_c$ which corresponds to the peak observed experimentally. The value of f_c is different for different gases providing selective detection of different species. If the gate voltage is swept across the Dirac point, the response of Graphene can be switched from n-type to p-type. We model such a situation by letting γ in Eq. (7) be a sinusoidal function of the gate voltage Vg which is directly related to time. We modify Eq. (7) as,

$$\sigma(t) = \sigma_0 + \gamma_0 \{a + (1-a)\cos(\omega_0 t)\}\delta N(t) \quad (11)$$

Where $0 \le a < 1$ is an asymmetry factor to account for the case where n-type and p-type conductivity values could be
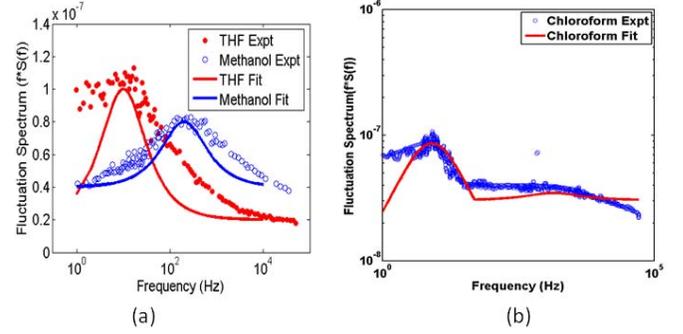

Fig. 1. Comparison of simulated fluctuation spectrum (noise spectral density multiplied by frequency Vs frequency) with published data [1] for (a) tetrahydrofuran (THF) and methanol (b) tetrahydrofuran and chloroform.

different; and ω_0 is the frequency of gate voltage modulation. When a = 0, it is perfectly symmetric meaning the n-type and p-type conductivities have equal magnitude. Increasing the value of a decreases the modulation strength.

Using the fourier transform relation given below [10],

$$FT\left(u(t)e^{-t/\tau}\cos(\omega_0 t)\right) = \frac{2\pi f_c + j\omega}{\omega_0^2 + (2\pi f_c + j\omega)^2} \quad (12)$$

we can write the power spectrum of component i corresponding to Eq. (10) as

$$S_{mod} = \frac{A}{f} + 2\pi \left| \frac{a\sqrt{B}}{2\pi f_c + j\omega} + \frac{(1-a)\sqrt{B}(2\pi f_c + j\omega)}{\omega_0^2 + (2\pi f_c + j\omega)^2} \right|^2 \quad (13)$$

Which upon rewriting becomes,

$$S_{mod} = \frac{A}{f} + \left| \frac{a\sqrt{B}}{f_c + jf} + \frac{(1-a)\sqrt{B}(f_c + jf)}{f_0^2 + (f_c + jf)^2} \right|^2 \quad (14)$$

We can obtain H_{mod} by multiplying Eq. (13) above with f. Consider the situation where graphene-FET is exposed to a mixture of three gases, namely, tetrahydrofuran (THF), chloroform and methanol.

III. RESULTS AND DISCUSSIONS

Experimental power spectra of Gr-FET in presence of methanol, chloroform and THF have been measured before [1]. Methanol and THF have widely separated peaks whereas the peaks for chloroform and THF are closely spaced. Therefore the ability to distinguish THF and chloroform would indicate the efficacy of selective detection with this approach. In Fig. 1 below, we use this data to find the appropriate parameter values for A, B and f_c for these three gases corresponding to the analytical model of power spectra given by Eq. (9). Such a comparison between experimental data and the Lorentzian model of Eq. (9) was not provided in previous work [6]. We see that, while the model exhibits a peak reminiscent of the experimentally observed one, the experimental linewidths are much broader than that of the model. The parameter values found best fitting to the experimental values are shown in Table I.

TABLE I
ESTIMATED PARAMETER (A, B, f_c) VALUES

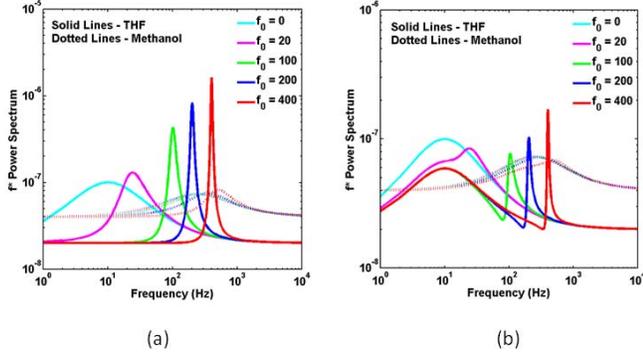| Parameters	Tetrahydrofuran	Methanol	Chloroform
A	2e-8	3.5e-8	4.73e-9
B	1.6e-6	1.5e-05	1.30e-6
f_c	10	240	8

The data are in Ae±b:=A*10$^{\pm b}$ format.

Fig. 2.   Enhancement of the fluctuation spectrum of THF and methanol for a = 0 (Fig. 2a) and a = 0.7 (Fig. 2b) for different values of the modulation frequency fo, namely, 0, 20, 100, 200 and 400 Hz.
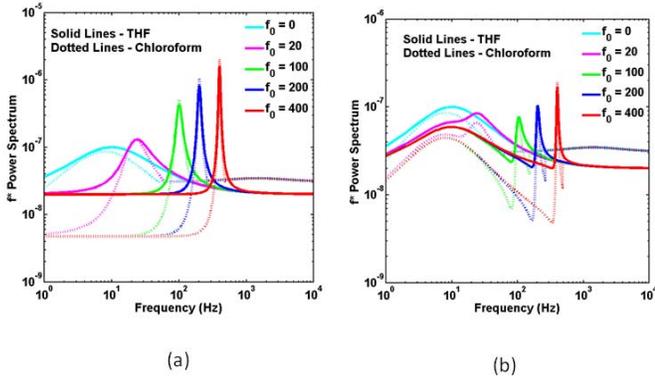

Fig. 3.   Enhancement of the fluctuation spectrum of THF and chloroform for a = 0 (Fig. 3a) and a = 0.7 (Fig. 3b) for different values of the modulation frequency fo, namely, 0, 20, 100, 200 and 400 Hz.

After obtaining the appropriate parameter values, we considered the effect of gate voltage modulation on H, the product of frequency and the power spectrum, which we refer to in this article as the fluctuation spectrum. We considered THF which has a peak position at 10 Hz and methanol which has a peak position at about 240 Hz. We calculated the quantity H, for various gate modulation frequencies starting from 0 to 400 Hz. The value at 0 Hz modulation is the baseline value without any modulation (i.e. the f_c term in Eq. 9), shown in Fig. 1 and measured experimentally in [1]. As we start increasing the modulation frequency, we see (Fig. 2 and Fig. 3) that the peak position of the fluctuation spectrum slowly starts moving towards the modulation frequency instead of the characteristic frequencies observed for the different gases. This would seem detrimental to the ability to selectively detect gases.
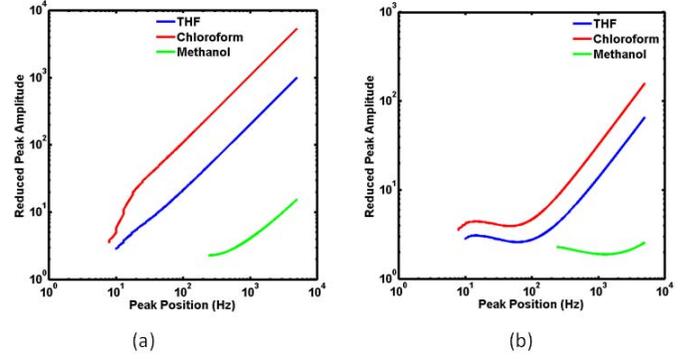

Fig. 4.   Variation of reduced peak amplitude with peak position for a = 0 (Fig. 4a) and a = 0.7 (Fig. 4b).

However, as we observe from Fig. 2 and Fig. 3, there is a selective amplification of the peak of the fluctuation spectrum. As we gradually increase the modulation frequency, the peak corresponding to THF and chloroform starts to rise while the peak corresponding to methanol is unaffected. As the modulation frequency continues to increase and becomes closer to the baseline peak frequency of methanol, the peak corresponding to methanol also starts to get amplified. This effect happens for the entire range of symmetry factors. Fig. 2 (a) and (b) show this effect for a = 0 and a = 0.7 respectively, which is in the decreasing order of modulation strength. Similar behaviour is also noticed in case of THF and chloroform and is shown in Fig 3. We can see that the spectra corresponding to choloroform can be clearly distinguished from that of THF even though their corner frequencies fc are similar as the peak amplitudes relative to the baseline is still quite distinct. As we see from these results, the amplification is directly dependent on the modulation strength and provides selective enhancement for different gases based on the parameters, A, B and fc mentioned in Eq. (14). Thus gases which have very closely spaced corner frequency peaks can also be distinguished.

The origin of this amplification is easy to understand from Eq. (14), considering the specific case of $a = 0$. From Eq. (10), we can see that the baseline peak value for $f_0 = 0$ is given by $A + B/2f_c$ as the peak occurs at $f = f_c$ for this function. Similarly, one can easily see that the maximum of the function in Eq. (14) will occur at $f^2 = f_0^2 + f_c^2$. When the modulation frequency is much larger than f_c, one can approximate the peak position to be at f_0 as we see in Fig 2(a), (b) and particularly in Fig. 4 where we see the peak position gradually become equal to the modulation frequency. Under this approximation we see that the peak value of Eq. (14) is given by $A + Bf_0/4f_c^2$, i.e. the value above the constant background A has been scaled by a factor $f_0/2f_c$. So gases with f_c less than f_0 will have their amplitudes enhanced while gases with f_c more than f_0 will be unaffected. The latter statement can be confirmed by considering the other limit of $f_c \gg f_0$ and peak position approximated by f_c. This is the origin of the selective enhancement of fluctuation amplitudes seen in Fig. 2 and 3.

As shown in Fig. 4, for a particular gas, the peak position starts shifting only when the modulation frequency approaches

close to its f_c value. For instance, as seen in Fig. 4, the peak position for methanol does not start shifting until the modulation frequency reaches around 100 Hz close to its f_c value of about 240 Hz. Therefore, even though for high modulation frequencies, the peak positions become indistinguishable for different gases, in the intermediate range their positions can still be distinguished. Further, as the fluctuation spectrum is also sensitive to the A and B parameters, by including the peak amplitude relative to a reference frequency (taken as 0 Hz here), gases with very close values of fc, such as THF and chloroform, can also be distinguished as shown in Fig. 4 which shows the evolution of peak position and relative peak amplitude as a function of increasing modulation frequency. THF and chloroform curves are close near their corner frequencies around 10 Hz. However, the gases can still be distinguished based on the peak position vs relative peak amplitude curve. A secondary effect that we observe from Fig. 2 and 3 is the narrowing of the peak linewidth which should enable a higher resolution for distinguishing peak frequencies corresponding to different gases.

IV. Conclusion

In summary, we have considered an extension of the fluctuation based sensing of gases where the conductance of a graphene field effect transistor is modulated using a sinusoidally varying gate voltage. We showed that this modulation scheme selectively amplifies the peaks of the fluctuation spectra. We believe that this effect could be used to enhance the fluctuation signals in mixtures where some of the constituents have concentrations lower than the threshold required for producing a peak above the 1/f background. The external gate voltage modulation will amplify the peak value and make it visible above the background.

References

[1] S. Rumyantsev, G. Liu, M. S. Shur, R. A. Potyrailo, and A. A. Balandin, "Selective gas sensing with a single pristine graphene transistor," *Nano Lett.*, vol. 12, pp. 2294–2298, Apr. 2012.

[2] F. Schwierz, "Graphene transistors," *Nature Nanotechnol.*, vol. 5, pp. 487–496, May 2010.

[3] D. Reddy, L. F. Register, G. D. Carpenter, and S. K. Banerjee, "Graphene field-effect transistors," *J. Phys. D, Appl. Phys.*, vol. 44, no. 31, pp. 1–20, Jul. 2011.

[4] B. Zhan *et al.*, "Graphene field-effect transistor and its application for electronic sensing," *Small*, vol. 10, no. 20, pp. 4042–4065, Jul. 2014.

[5] K. Matsumoto, Ed., *Frontiers of Graphene and Carbon Nanotubes*, 1st ed., Tokyo, Japan: Springer, 2015.

[6] K. S. Novoselov *et al.*, "Electric field effect in atomically thin carbon films," *Science*, vol. 306, no. 5696, pp. 666–669, Oct. 2004.

[7] U. Latif and F. L. Dickert, "Graphene hybrid materials in gas sensing applications," *Sensors*, vol. 15, no. 12, pp. 30504–30524, 2015.

[8] G. Korotcenkov, "Metal oxides for solid-state gas sensors: What determines our choice," *Mater. Sci. Eng. B*, vol. 139, pp. 1–13, Apr. 2007.

[9] S. Rumyantsev, G. Liu, R. A. Potyrailo, A. A. Balandin, and M. S. Shur, "Selective sensing of individual gases using graphene devices," *IEEE Sensors J.*, vol. 13, no. 8, pp. 2818–2822, Aug. 2013.

[10] A. V. Oppenheim and A. S. Willsky, *Signals and Systems*, 2nd ed., A. V. Oppenheim, Ed. Upper Saddle River, NJ, USA: Prentice-Hall, 1996.

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