



CHARACTERIZATION OF HETEROGENEOUS SENSING LAYERS IN GRAPHENE-BASED GAS SENSORS

STEVAN ANDRIĆ

University of Belgrade - Institute of Chemistry, Technology and Metallurgy - National Institute of the Republic of Serbia, Belgrade, Serbia, stevan@nanosys.ihtm.bg.ac.rs

IVANA JOKIĆ

University of Belgrade - Institute of Chemistry, Technology and Metallurgy - National Institute of the Republic of Serbia, Belgrade, Serbia, ijokic@nanosys.ihtm.bg.ac.rs

MILOŠ FRANTLOVIĆ

University of Belgrade - Institute of Chemistry, Technology and Metallurgy - National Institute of the Republic of Serbia, Belgrade, Serbia, frant@nanosys.ihtm.bg.ac.rs

KATARINA RADULOVIĆ

University of Belgrade - Institute of Chemistry, Technology and Metallurgy - National Institute of the Republic of Serbia, Belgrade, Serbia, kacar@nanosys.ihtm.bg.ac.rs

MARKO SPASENOVIĆ

University of Belgrade - Institute of Chemistry, Technology and Metallurgy - National Institute of the Republic of Serbia, Belgrade, Serbia, spasenovic@nanosys.ihtm.bg.ac.rs

Abstract: Graphene-based sensors have a great potential for applications in public and personal health protection, including defense and security fields. However, sensitivity and selectivity of such sensors are inherently dependent on adsorption properties of the graphene sensing layer, which is typically of heterogeneous morphology and/or of heterogeneous chemical composition due to intentionally introduced functionalizing elements or spontaneously adsorbed molecules during sensor fabrication or operation. Therefore, characterization and optimization of sensing layers is extremely important for achieving high sensing performance. In this work, we present a method for characterization of the heterogeneous sensing layer by using the frequency domain analysis of the sensor output signal. The method is based on the mathematical model we devised. Here, the model is presented in detail for the case of a surface with three types of adsorption sites, and then the method is applied for extraction of parameters that characterize adsorption properties of a graphene sensing layer.

Keywords: gas sensor, graphene, heterogeneous sensing layer, sensing surface characterization.

1. INTRODUCTION

Gas sensors are of vital importance for public and personal health protection, including defense and security fields. Graphene-based sensors have a great potential for such applications [1-4]. It stems from unique properties of graphene, such as a large specific surface area exposed to the adsorption of gas particles, and a pronounced change in its electrical, mechanical and optical parameters caused by gas adsorption, which results in a measurable sensor response even to extremely low adsorbed quantities [1]. The fast response of gas sensors based on graphene, and their applicability as low-power, miniature and portable monitoring devices, make them convenient for real time and in-situ gas detection. However, sensitivity and selectivity of such sensors (being adsorption-based) inherently depend on adsorption properties of the sensing layer, which is typically of heterogeneous morphology and/or of heterogeneous chemical composition due to

intentionally introduced functionalizing elements or spontaneously adsorbed molecules during sensor fabrication or operation. Therefore, characterization and optimization of sensing layers is extremely important for achieving high sensing performance.

Among graphene-based gas sensors, heterogeneity of the sensing surface morphology is especially pronounced in those with sensing layers obtained by the liquid phase exfoliation (LPE) method [5, 6]. LPE graphene consists of randomly arranged flakes with an abundance of highly reactive edges, which significantly increases graphene's capability for capturing of gas particles, and makes the material suitable for gas sensing. On the other hand, due to the existence of adsorption sites on both the edges and the basal planes of flakes, LPE graphene is a heterogeneous sensing material, which must be kept in mind during the evaluation and optimization of sensing performance, and the analysis of the measurement data.

In this paper, we present a method for characterization of the heterogeneous sensing layers of gas sensors. The method consists of the frequency domain analysis of the sensor output signal, and it is based on the mathematical model we devised [7, 8]. Here, we present in detail the model for the case of heterogeneous sensing layer with three types of adsorption sites. Then we illustrate the application of the model in the method for characterization of the surface of LPE graphene sensor for the detection of carbon-dioxide.

2. A MATHEMATICAL MODEL FOR THE FREQUENCY DOMAIN ANALYSIS OF A SENSOR OUTPUT SIGNAL

The sensing layer heterogeneity assumes that there is more than one type of adsorption sites, and that sites of different types differ in the affinities towards gas particles. When there are three types of adsorption sites, a sensor output signal is determined by

$$s = r_1 N_1 + r_2 N_2 + r_3 N_3 \quad (1)$$

where N_i (i is 1, 2 or 3) is the number of adsorbed particles on type i binding sites at the moment t , and r_i is the weight factor, representing the mean contribution to the sensor response of a single gas particle adsorption on a type i site. The output signal of resistive sensors is the change of the sensing layer conductance, which is proportional to the number of charge carriers, s_w , generated in the layer by gas adsorption, i.e. through the charge transfer between graphene and adsorbed gas particles. Therefore, Eq. (1) can be expressed as

$$s = u s_w = u(w_1 N_1 + w_2 N_2 + w_3 N_3) \quad (2)$$

w_i being the weight factor, equal to the mean number of charge carriers induced in a sensing material per a gas molecule adsorbed on a type i site, and u is the conversion factor of the total number of generated charge carriers to the resistance change.

The numbers of adsorbed particles changes through the processes of adsorption and desorption according to the equations [9]

$$\frac{dN_i}{dt} = k_{api} p (N_{mi} - N_i) - k_{di} N_i, \quad i \text{ is } 1, 2 \text{ or } 3 \quad (3)$$

where p is the gas pressure, N_{mi} is the number of type i adsorption sites on the sensing surface, and the corresponding adsorption and desorption rate constants for a given gas, k_{api} and k_{di} , equal

$$k_{api} = \frac{\alpha_i}{n_{mi}} \frac{1}{\sqrt{2\pi M k_B T}}, \quad k_{di} = \frac{1}{\tau_i} = \frac{1}{\tau_{0i} e^{E_{di}/(RT)}} \quad (4)$$

Here, α_i is the sticking coefficient, $n_{mi} = N_{mi}/A_i$ is the surface density of sites that cover the part of the sensing surface of the area A_i , M is the mass of a single gas particle, T is the temperature, τ_{0i} is the period of thermal vibrations of the adsorbed particle (typically of the order of 10^{-14} - 10^{-12} s), E_{di} is the desorption energy, k_B is the

Boltzmann constant, and R is the gas constant. Solving Eqs. (3) in the steady state ($dN_i/dt=0$) yields the expressions for the number of adsorbed particles on three types of sites

$$N_{Si} = \frac{b_i p}{b_i p + 1} N_{mi} \quad (5)$$

and for the parameter

$$b_i = \frac{k_{api}}{k_{di}} = \frac{\alpha_i \bar{\tau}_i}{n_{mi}} \frac{1}{\sqrt{2\pi M k_B T}} \quad (6)$$

The frequency domain analysis of a sensor output signal starts from the Langevin equations which describe the fluctuations of the numbers of adsorbed particles ΔN_i around the corresponding steady-state values (these inevitable stochastic fluctuations are caused by the random nature of adsorption-desorption processes)

$$\frac{d\Delta N_i}{dt} = -\frac{1}{\tau_i} \Delta N_i + \xi_i \quad (7)$$

where

$$\tau_i = \frac{\bar{\tau}_i}{b_i p + 1} \quad (8)$$

and ξ_i is a random source function. Eqs. (7) are solved in the frequency domain in order to obtain the power spectral density (PSD) of fluctuations of the number of particles adsorbed on each type of sites

$$S_{Ni} = \frac{4N_{Si} \tau_i^2 / \bar{\tau}_i}{1 + f^2 / f_i^2} \quad (9)$$

The characteristic frequencies of the spectrum are

$$f_i = \frac{1}{2\pi\tau_i} = \frac{1}{2\pi\bar{\tau}_i} \left(\frac{\alpha_i \bar{\tau}_i}{n_{mi}} \frac{1}{\sqrt{2\pi M k_B T}} p + 1 \right) \quad (10)$$

The PSD of fluctuations of the output signal equals

$$S = r_1^2 S_{N1} + r_2^2 S_{N2} + r_3^2 S_{N3} \quad (11)$$

since fluctuations of the number of adsorbed particles on different types of adsorption sites are statistically independent. Based on Eq. (2)

$$S = u^2 S_w = u^2 (w_1^2 S_{N1} + w_2^2 S_{N2} + w_3^2 S_{N3}) \quad (12)$$

where S_w is the PSD of the fluctuations of the number of carriers. After substituting Eqs. (9) in Eq. (12), and performing mathematical transformations, we obtain

$$S_w = S_{w,LF} \frac{(1 + f^2 / f_1^2)(1 + f^2 / f_2^2)}{(1 + f^2 / f_1^2)(1 + f^2 / f_2^2)(1 + f^2 / f_3^2)} \quad (13)$$

where the two remaining characteristic frequencies of the power spectrum are given by the system of equations

$$f_I^2 f_{II}^2 = \frac{(K_1 + K_2 + K_3) f_1^2 f_2^2 f_3^2}{K_1 f_1^2 + K_2 f_2^2 + K_3 f_3^2} \quad (14)$$

$$f_I^2 + f_{II}^2 = \frac{(K_1 + K_2) f_1^2 f_2^2 + (K_2 + K_3) f_2^2 f_3^2 + (K_1 + K_3) f_1^2 f_3^2}{K_1 f_1^2 + K_2 f_2^2 + K_3 f_3^2} \quad (15)$$

and the spectrum low frequency magnitude is

$$S_{w,LF} = K_1 + K_2 + K_3 \quad (16)$$

$$K_i = \frac{4w_i^2 N_{Si} \tau_i^2}{\bar{\tau}_i} \quad (17)$$

In order to obtain the expressions for the sensing layer parameters that determine its adsorption properties, we perform the following mathematical derivations. First, we introduce the designations

$$B_1 = \frac{f_I^2 f_{II}^2}{f_1^2 f_2^2 f_3^2}, \quad B_2 = f_I^2 + f_{II}^2 \quad (18)$$

After dividing both the numerator and the denominator of the expressions on the right side of Eqs. (14) and (15) by N_{m2} (here we have chosen N_{m2} , otherwise it can be any N_{mi}), and using Eqs. (18), we obtain

$$B_1 = \frac{K_{1p} v_{12} + K_{2p} + K_{3p} v_{32}}{K_{1p} v_{12} f_1^2 + K_{2p} f_2^2 + K_{3p} v_{32} f_3^2} \quad (19)$$

$$B_2 = \left[(K_{1p} v_{12} + K_{2p}) f_1^2 f_2^2 + (K_{2p} + K_{3p} v_{32}) f_2^2 f_3^2 + (K_{1p} v_{12} + K_{3p} v_{32}) f_1^2 f_3^2 \right] / (K_{1p} v_{12} f_1^2 + K_{2p} f_2^2 + K_{3p} v_{32} f_3^2) \quad (20)$$

where

$$K_{ip} = \frac{K_i}{N_{mi}} = 4w_i^2 \frac{b_i p}{b_i p + 1} \frac{\tau_i^2}{\bar{\tau}_i} \quad (21)$$

while v_{12} and v_{32} are the relative abundances of different types of adsorption sites on the sensing surface

$$v_{12} = \frac{N_{m1}}{N_{m2}}, \quad v_{32} = \frac{N_{m3}}{N_{m2}} \quad (22)$$

These parameters are used to characterize a sensing layer heterogeneity, and they are obtained from Eqs. (19) and (20) in the form

$$v_{12} = \frac{f_2^2 - f_3^2}{f_3^2 - f_1^2} \frac{f_1^2 + B_1 f_2^2 f_3^2 - B_2}{f_2^2 + B_1 f_1^2 f_3^2 - B_2} \frac{K_{2p}}{K_{1p}} \quad (23)$$

$$v_{32} = - \frac{f_2^2 - f_1^2}{f_3^2 - f_1^2} \frac{f_3^2 + B_1 f_1^2 f_2^2 - B_2}{f_2^2 + B_1 f_1^2 f_3^2 - B_2} \frac{K_{2p}}{K_{3p}} \quad (24)$$

The ratio of the number of type 1 sites and the number of

sites of the other two types is

$$v_1 = \frac{N_{m1}}{N_{m2} + N_{m3}} = \frac{v_{12}}{1 + v_{32}} \quad (25)$$

The total sensing area A consists of the parts A_i , containing different adsorption sites. Thus

$$A = A_1 + A_2 + A_3 = N_{m1} / n_{m1} + N_{m2} / n_{m2} + N_{m3} / n_{m3} \quad (26)$$

$$A_1 = \frac{v_{12} n_{m2} n_{m3}}{v_{12} n_{m2} n_{m3} + n_{m1} n_{m3} + v_{32} n_{m1} n_{m2}} A \quad (27)$$

$$A_2 = \frac{n_{m1} n_{m3}}{v_{12} n_{m2} n_{m3} + n_{m1} n_{m3} + v_{32} n_{m1} n_{m2}} A \quad (28)$$

$$A_3 = \frac{v_{32} n_{m1} n_{m2}}{v_{12} n_{m2} n_{m3} + n_{m1} n_{m3} + v_{32} n_{m1} n_{m2}} A \quad (29)$$

According to Eqs. (12) and (13), the PSDs S and S_w are proportional, and they have the same five characteristic frequencies (f_1, f_2, f_3, f_I and f_{II}). Thus, if these frequencies are used as a source of information of the sensing surface adsorption properties, it is convenient to use S_w instead of S in the analysis, because in that way it is not necessary to know the value of the parameter u , which depends on the geometric parameters of the sensing layer [10].

3. A METHOD FOR CHARACTERIZATION OF HETEROGENEOUS SENSING LAYERS

Characterization of a heterogeneous sensing layer encompasses the determination of the number and surface density of each type of sites on the sensing surface, which have a certain affinity for gas particles binding. These parameters, as well as the relative abundance of different types of adsorption sites, determine the dominant adsorption mechanism, and influence sensor characteristics such as the response magnitude, time response, sensor sensitivity and selectivity. The method that enables such characterization is based on the mathematical model presented in Section 2, and we describe its application for a LPE graphene sensor characterization, since the LPE graphene sensing layer naturally contains at least two types of adsorption sites.

For completely reversible adsorption, the site affinity for gas particles binding is described by the adsorption/desorption energy. Reversible adsorption is desirable in gas sensing applications, because it enables sensor reusability. The method we present, being based on the frequency domain analysis of sensor signal fluctuations, takes into account only the surface sites where the reversible adsorption occurs (the irreversible adsorption does not contribute to the fluctuations of the number of adsorbed particles, so it is not “visible” in the frequency domain after the establishment of the steady-state of all adsorption processes occurring on the sensing surface). Therefore, it is reasonable to assume the existence of three types of adsorption sites with reversible

adsorption processes on the LPE graphene surface: the sites on the edges of the graphene flakes (type 1 sites), and two types of functionalized sites on the basal planes of the flakes – those that are native, i.e. unoccupied by adsorbates (type 2 sites), and those that are already occupied by atoms/molecules of some reactive gas species from the environment (type 3 sites). Apart from the gas pressure and temperature values that are set and then kept constant, the characterization method uses the desorption energies and the weight factors for all types of adsorption sites as input parameters. In the case of 2D materials, the values of these parameters are usually obtained by the density functional theory (DFT) or other calculation methods [4, 11]. For the illustration of the method, we use the parameter values from the literature, which are obtained by DFT calculations for the reversible adsorption of CO₂ on the edges of graphene nanoribbons [12], and on Fe-functionalized graphene [13], where some of the functionalized basal plane sites are occupied by O₂ molecules, but they still can bind carbon-dioxide molecules: the desorption energies are $E_{d1}=19$ kcal/mol, $E_{d2}=12.5$ kcal/mol, and $E_{d3}=8.07$ kcal/mol, while the weight factors for a resistive sensor, expressed as the mean number of charge carriers induced in graphene per adsorbed CO₂ molecule, equal $w_1=0.9$, $w_2=0.02$, and $w_3=0.1$. Gas pressure $p=0.1$ Pa, the temperature $T=300$ K, and the sensing surface area $10\text{ mm} \times 10\text{ mm}$ are used in the analysis.

The method consists of the following steps:

1. When a sensor response reaches the steady state for a given gas pressure and temperature, the PSD of the sensor output signal is experimentally determined. Figure 1 shows the simulated PSD of fluctuations of the number of charge carriers in graphene for the above given parameter values.

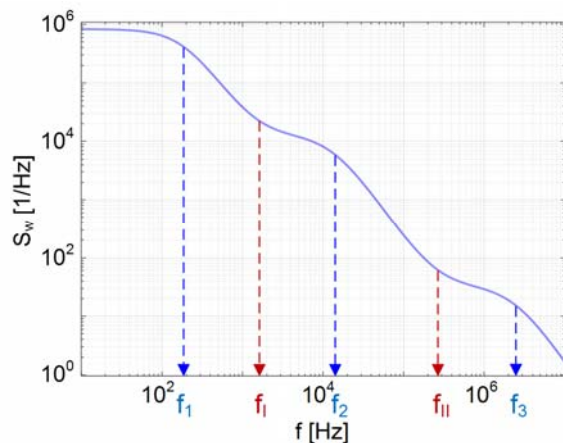


Figure 1. The power spectral density of the number of charge carriers in LPE graphene, caused by inherently random adsorption-desorption processes of carbon-dioxide molecules on the graphene sensing surface with three types of adsorption sites. The characteristic frequencies are shown.

2. The characteristic frequencies are determined from the experimentally obtained PSD, in accordance with Eq. (13), which for the example presented in Figure 1 yields $f_1=183$ Hz, $f_2=1.32 \times 10^4$ Hz, $f_3=2.35 \times 10^6$ Hz, $f_{i1}=1.65 \times 10^3$

Hz and $f_{i1}=2.62 \times 10^5$ Hz.

3. The surface density of each type of adsorption sites, n_{mi} , is uniquely determined by the frequency f_i , according to Eqs. (10), (8) and (6); thus, their values are obtained by using the experimentally obtained f_1 , f_2 and f_3 and the mentioned equations. For the given example: $n_{m1}=2 \times 10^{18}$ 1/m² and $n_{m2}=n_{m3}=4 \times 10^{17}$ 1/m².

4. The parameters B_1 and B_2 are calculated based on Eqs. (18) and the experimentally determined frequencies f_1 , f_2 , f_3 , f_{i1} and f_{i2} . The time constants τ_i and the parameters b_i are calculated after substituting the values for f_1 , f_2 and f_3 in Eqs. (10) and (8), respectively; then the parameters K_{ip} are calculated from Eq. (21). Consequently, the relative abundances of different types of adsorption sites are obtained by using Eqs. (23)-(25), which in our example yields $v_{12}=0.02$, $v_{32}=3$ and $v_1=0.005$.

5. The areas covered by each type of adsorption sites can now be obtained from Eqs. (27)-(29). In the analyzed example, $A_1=1 \times 10^{-7}$ m², $A_2=2.5 \times 10^{-5}$ m² and $A_3=7.49 \times 10^{-5}$ m², which means that the adsorption sites of the types 1, 2 and 3 occupy 0.1%, 25% and 74.9% of the total sensing surface, respectively.

6. Finally, the numbers of adsorption sites of different types are obtained as $N_{mi}=n_{mi}A_i$. Therefore, $N_{m1}=2 \times 10^{11}$, $N_{m2}=1 \times 10^{13}$ and $N_{m3}=3 \times 10^{13}$ in the given example.

The results of the sensing surface characterization by using the described method are summarized in Table 1.

Table 1. LPE graphene parameters describing heterogeneous adsorption properties of its surface towards CO₂; three types of sites are considered (A is the total sensing area, N_m is the total number of adsorption sites)

Site Parameter	Type 1 = Edge sites	Type 2 = Basal Fe sites	Type 3 = Basal Fe+O ₂ sites
Effective sensing area covered % of A	1×10^{-7} m ² 0.1% A	2.5×10^{-5} m ² 25% A	7.49×10^{-5} m ² 74.9% A
Surface density of adsorption sites	2×10^{18} 1/m ²	4×10^{17} 1/m ²	4×10^{17} 1/m ²
Number of adsorption sites % of N_m	2×10^{11} 0.497% N_m	1×10^{13} 24.876% N_m	3×10^{13} 74.627% N_m

4. CONCLUSIONS

The analysis of a gas sensor output signal in the frequency domain has been proven as an efficient tool for characterization of sensing layer adsorption properties. For the given adsorption/desorption energies for each type of adsorption sites, and the conversion factors that relate the binding of target molecules to the change of a sensor measurable parameter (which can be obtained by using the density functional theory or other calculation methods), the mathematical model and method presented

in this paper enable the characterization in terms of the abundance of various adsorption site types on the sensing surface, which is a unique property of a given sensor. It cannot be reliably predicted by other methods, so it must be determined experimentally. The significance of the model and method stem from the fact that real sensing layers (including those based on graphene) are not ideally homogeneous, which necessitates their characterization prior to their use for sensing, because the adsorption properties inherently affect gas sensor characteristics such as sensitivity, selectivity and the minimal detectable concentration.

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