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Influence of Reduction in the Heat of Adsorption on Noise Characteristics of Sensors

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Abstract: Recently, noise spectroscopy has proposed as powerful method for extracting information from gas sensors [1]. In this paper, we propose to take into account the phenomenon of a reduction in the heat of adsorption considered earlier and also use results of Langmuir's theory for oxygen to calculate the noise for other type of gases. *Copyright © 2012 IFSA.*

Keywords: Adsorption, Desorption, Chemisorption, Gas sensor.

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1. Introduction

The sensitivity of gas sensors was earlier measured by classical method-comparison the resistance of sensors in gas media and air. In [1-3] we reported results of the experimental study of low-frequency noise characteristics of sensors. We compared data for different Figaro TGS sensors as well as our sol-gel H2 tin dioxide and porous silicon sensors. Higher sensitivity of spectral dependence of noise to gas concentration in comparison with classical method of the measurements of gas sensing by a change in the Ohmic resistance part of current-voltage characteristics of samples allows using such spectral dependence of noise powerful method for determination of gas concentration in the air or environment. In this paper, we propose to take into account the phenomenon of a reduction in the heat of adsorption considered earlier [4] and also use results of Langmuir's theory for oxygen to calculate the noise for other type of gases.

2. Theory of Adsorption

When an oxygen molecule is approaching the surface of an *n*-type semiconductor oxide like SnO_2, the probability of the trapping of conduction electron from the semiconductor is the occupation probability of the bandgap acceptor level $E_a = A - W_\phi$, where A is the electron affinity of the gas molecule and W_ϕ the semiconductor work function. This probability is given by Fermi-Dirac distribution function:

$$f_n(E_a) = \frac{1}{1 + (1/g_a)\exp[(E_a - E_F)/kT]}, \tag{1}$$

where E_F is the semiconductor's Fermi level and g_a is the degeneration degree of the impurity state introduced by the acceptor level E_a, k is the Boltzmann constant, T is the temperature. In the case of an acceptor level, the degeneration degree is equal to $g_a=1/2$. Actually f_n essentially changes only on low temperatures (0-100K) and at working temperatures we can consider it is a constant.

The method for gas detection in Langmuir's theory is the calculation of the Power Density of Spectrum (PDS) of fluctuation of the electrical conductance introduced by adsorption-desorption particles. Considering the adsorption kinetics for the case of the charging of the surface by a one-electron gas, in the framework of usual theory [5] the kinetic equation may be written in the form:

$$\frac{dN}{dt} = \alpha p\left(N^* - N\right) - \beta N, \tag{1}$$

where

$$\alpha = \frac{\aleph \partial}{\sqrt{2\pi m k T}}, \beta = \frac{1}{\tilde{\tau}}. \tag{2}$$

Here N is the quantity of adsorbed gas atoms per unit area of the surface of the adsorption layer, N^* is the number of adsorption centers per unit area, p is the partial gas pressure, $\aleph$ is the probability, that a molecule approaching an adsorption center will be fixed (probability of a holding of adsorbed molecule on the adsorption center), m and ∂, respectively the adsorbed molecule mass and effective area, t is the time, and $\tilde{\tau}$ denotes the average residence time, given by [5]:

$$\tilde{\tau} = \tau_0 \exp\left(\frac{E_d}{RT}\right), \tag{3}$$

where τ_0 is the period of thermal vibrations normal to the surface of the adsorbed molecule, R is the gas constant and E_d is the adsorption or desorption energy.

Langmuir's theory for PDS of the free electron's density fluctuations gives

$$S_{\delta n}\left(f\right) = 4\frac{\left(f_n\left(A - W_\phi\right)\right)^2}{d^2}\beta\frac{\alpha p}{\alpha p + \beta}N^*\frac{\tau^2}{1 + 4\pi^2 f^2 \tau^2}, \tag{4}$$

where d is the thickness of the sensing layer. At the adsorption-desorption equilibrium, the whole sensor's conductance is expressed by:

$$G = e\mu_n n\frac{s}{L} = e\mu_n\frac{s}{L}\left(n_0 + \delta n\right), \tag{5}$$

where e and μ_n are the electron charge and mobility, s and L, respectively the cross-section area and length of the sensing layer, n_0 is the density of free electrons at the adsorption-desorption equilibrium. In this case the PDS of the fluctuation of the electrical conductance will be expressed as:

$$S_{\delta G}(f)=\left(e\mu_n\frac{s}{L}\right)^2 S_{\delta n}(f)=\left(e\mu_n\frac{s}{Ld}\right)^2\frac{H_0}{1+f^2/f_c^2}, \tag{6}$$

where

$$H_0=4\left(f_n\left(A-W_\phi\right)\right)^2\beta\frac{\alpha p}{\alpha p+\beta}N^*\tau^2, \tag{7}$$

$$f_c=\frac{1}{2\pi\tau}=\frac{\alpha p+\beta}{2\pi}=\frac{1}{2\pi}\left[\tau_0^{-1}\exp\left(\frac{-E_d}{RT}\right)+\frac{\aleph\partial p}{\sqrt{2\pi mkT}}\right]. \tag{8}$$

The PDS of the fluctuation of the free electrons density was calculated for oxygen chemisorption on the surface of a SnO_2 sensor (Fig. 1). The gas partial pressure p was fixed at 0.2 atm. (2×10^4 Pa). The adsorbed molecule effective area ∂ was evaluated using the van der Waals coefficient b derived from gas triple point [6]. For metal-oxide systems and in particular in SnO_2, the present knowledge about numerical values of desorption energy is rather poor. We were forced to use estimation for adsorption energy $E_d=2eV$ [7]. The chemisorption probability value was fixed at 1. The number of chemisorption sites per unit surface area is estimated to $N^*=10^{15}cm^{-2}$.

Eq. 5 and Fig. 1 shows that oxygen chemisorption generates a fluctuation in the sensor's conductance which is a Lorentzian-like noise spectrum with a characteristic corner frequency f_c and low frequency magnitude H_0.

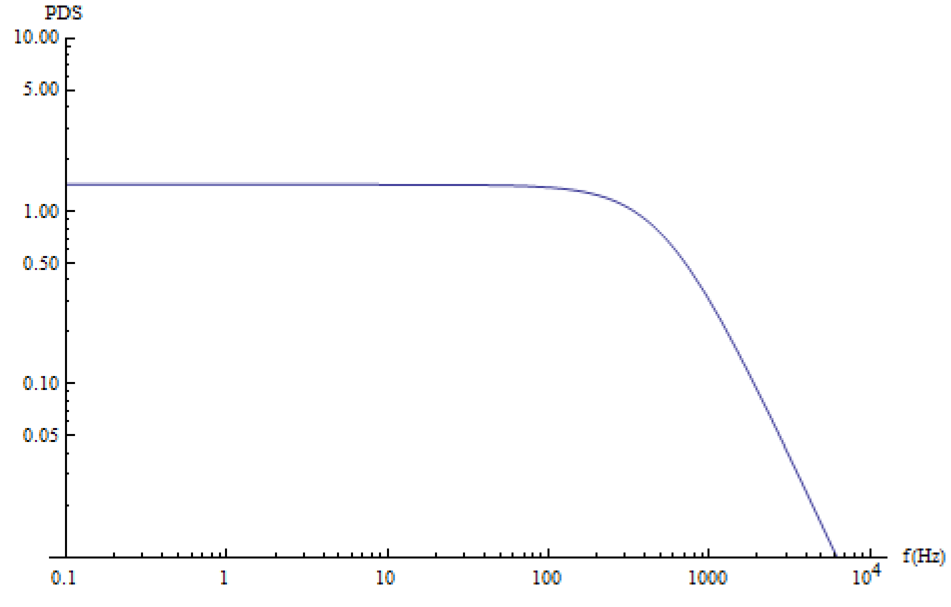

Fig. 1. PDS of the fluctuation of the free electrons density calculated for oxygen adsorbed on the surface of a metaloxide sensor at 373K.

For fixed sensor geometry the term $(e\mu_n s/Ld)^2$ is a constant. Actually Eq. 4 contains 2 independent parts which means that we can analyze them separately and at the end combine them into Eq. 4 to have the final frequency dependence of PDS of the fluctuation of the electrical conductance on the surface of a SnO_2. Temperature dependences of low frequency magnitude and corner frequency are shown in Fig. 2 and in Fig. 3 respectively.

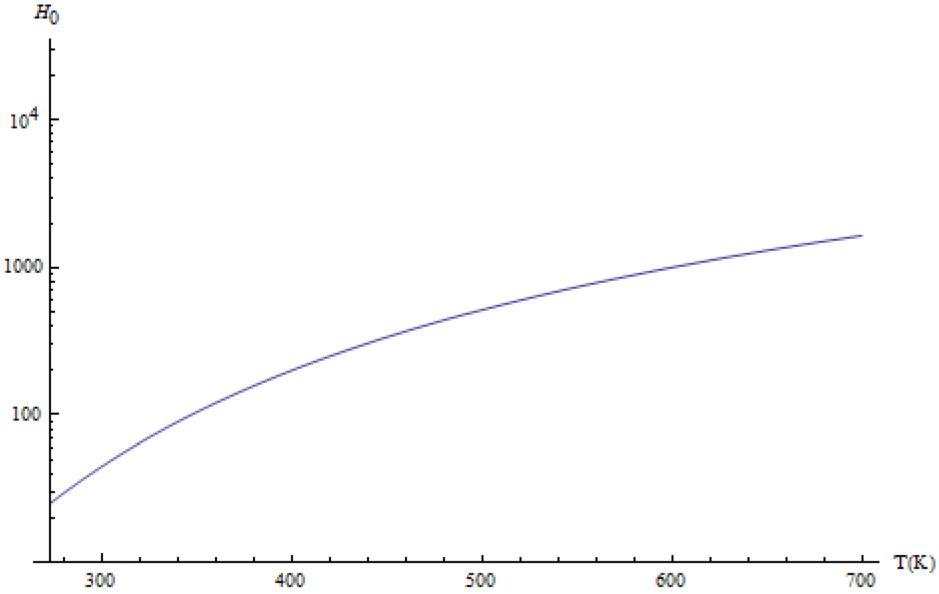

Fig. 2. Temperature dependence of low frequency magnitude of the PDS of the fluctuation of the free electrons density for oxygen adsorbed on SnO_2.

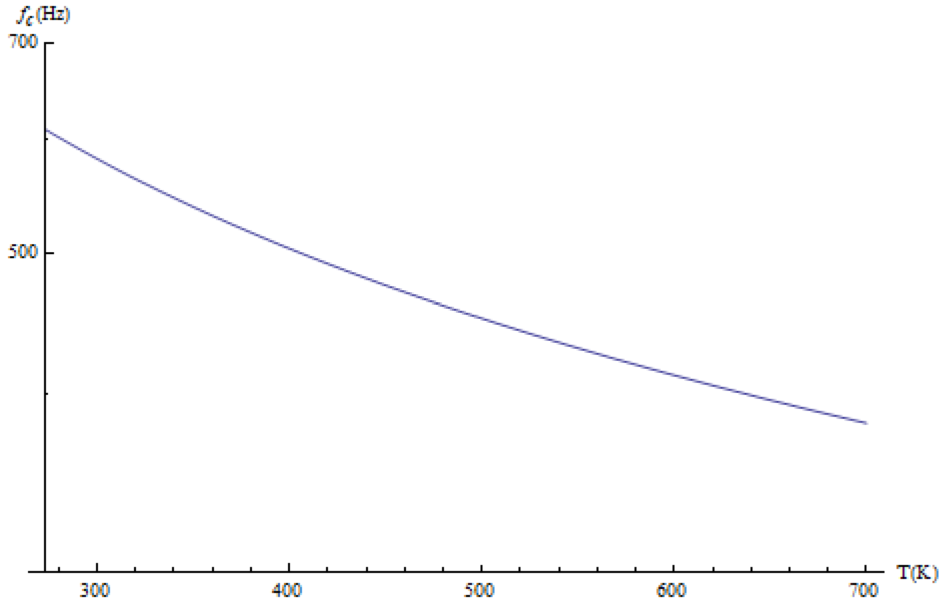

Fig. 3. Temperature dependence of corner frequency of the PDS of the Fluctuation of the free electrons density for oxygen adsorbed on SnO_2.

3. Influence of Reduction in Heat of Adsorption

Considering the case of a reduction in heat of adsorption the kinetic equation will be:

$$\frac{dN}{dt} = \alpha p\left(N^* - N\right) - \beta' N \,, \tag{9}$$

where

$$\beta' = \beta_0 \exp\left(\frac{\eta N}{kT}\right), \eta = 2\pi e^2 R_s. \tag{10}$$

In Eq. 10 R_S is the sensor's radius. This equation indicates that a number of molecules, leaving the semiconductor surface and passing in the gas phase, increases $\exp(\eta N/kT)$ times compare with the usual case described by the Langmuirian model. In order to understand influence of η on corner frequency and low frequency magnitude, we need to analyze the new formulas. It is easy to obtain that they can be written as:

$$H_0 = 4\left(f_n\left(A - W_\phi\right)\right)^2 \beta_0 \exp\left(\frac{\eta N}{kT}\right) N_0 \tau^2, \tag{11}$$

$$f_c = \frac{1}{2\pi}\left[\tau_0^{-1}\exp\left(\frac{-E_d}{R_g T}\right)\exp\left(\frac{\eta N}{kT}\right) + \frac{\aleph \partial p}{\sqrt{2\pi mkT}}\right]. \tag{12}$$

We can see from Eq. 11 that the value of low frequency magnitude is $\exp(\eta N/kT)$ times higher than the low frequency magnitude in Langmuirian model. Fig. 4 illustrates the temperature dependence of low frequency magnitude with different values of $(\eta N / kT)$ (0, 1, 2, 3).

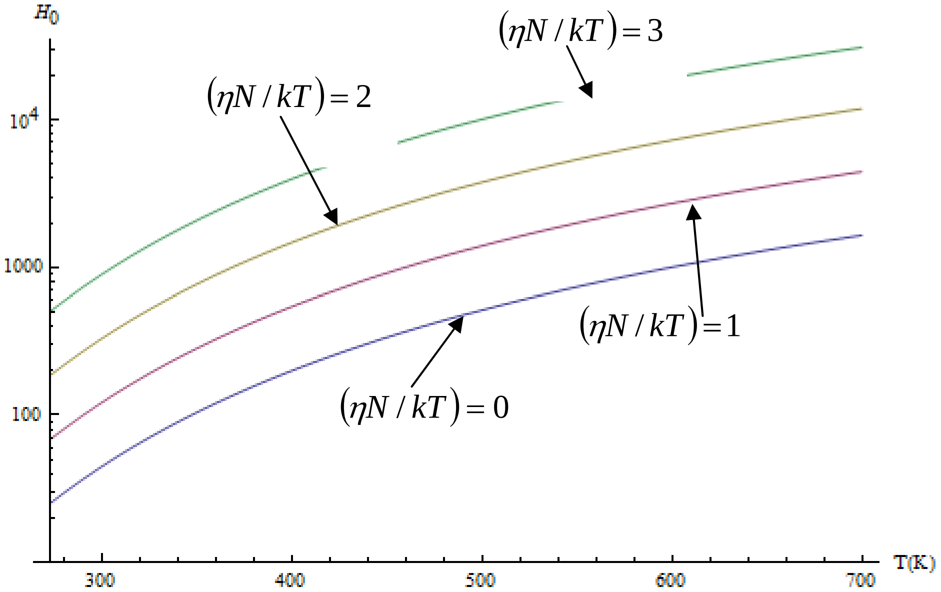

Fig. 4. Temperature dependence of low frequency magnitude for different values of $(\eta N / kT)$.

Temperature dependence of low frequency magnitude f_c on different values of $(\eta N / kT)$ is shown in Fig. 5.

All plots are very close each other at room temperature and because of which they are overlapped in that area. It means that at room temperatures we can consider f_c as a constant. Using these 2 figures and Eq. 4, we will obtain the PDS for different values of $(\eta N / kT)$ (Fig. 6). As we can see, the change in plots depends only on low frequency magnitude which determines the maximum value of PDS of the fluctuation of free electrons density.

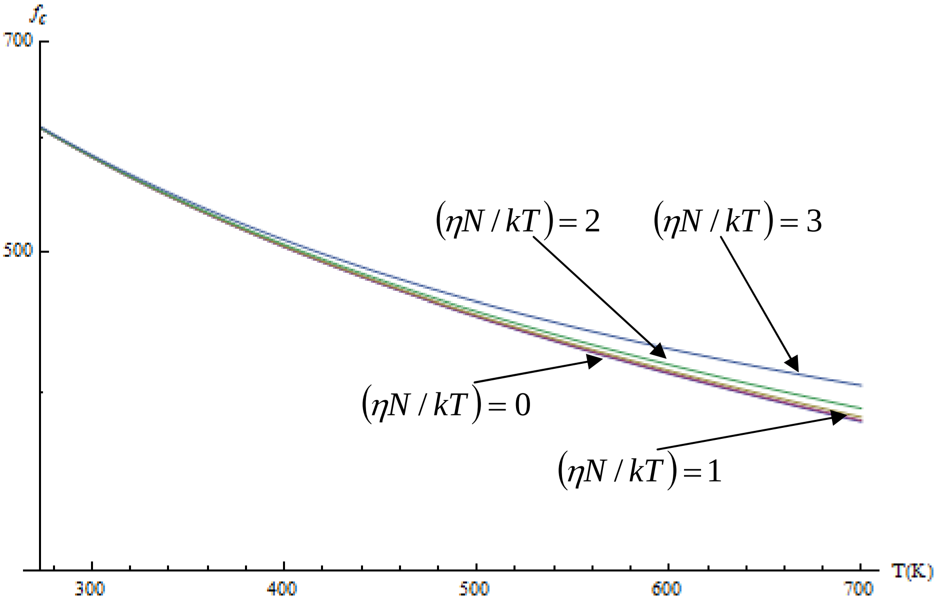

Fig. 5. Temperature dependence of corner frequency for different values of $(\eta N / kT)$.

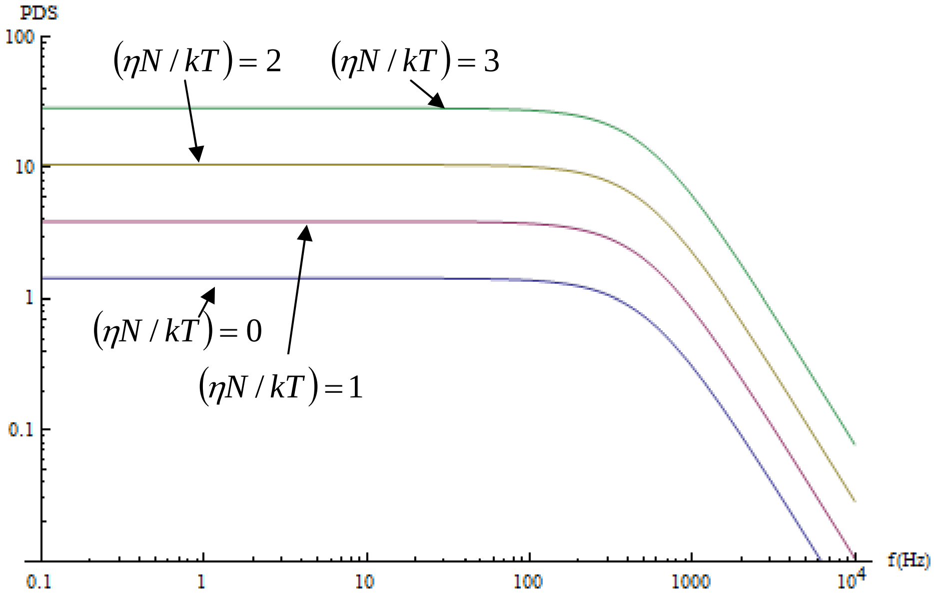

Fig. 6. PDS of the fluctuation of the free electrons density calculated for oxygen adsorbed on the surface of a metaloxide sensor at 373K for different values of $(\eta N / kT)$.

4. Adsorption-desorption Theory for Different Gases

There is an interest to make sensors which can detect different types of gases. Actually the theory described above was calculated only for oxygen and question arises how these formulas can be modified if we have hydrogen or another gas instead of oxygen. In order to modify these formulas that they can describe each type of gas, in these formula we need to separate parameters which are describing the gas. Let us start with the case of low frequencies. For simplicity, we will take hydrogen to compare with oxygen. At working temperatures $\alpha p >> \beta$ and for Eq. 7 we will have the following expression:

$$H_0 = 4\left(f_n\left(A - W_\phi\right)\right)^2 \frac{\beta}{(\alpha p)^2} N^* = const\frac{\beta}{(\alpha p)^2} = const\frac{2\pi mkT}{(\aleph \partial p)^2}\exp\left(-\frac{E_d}{RT}\right) = const\frac{m}{(\partial p)^2}. \tag{13}$$

The relationship of low frequency magnitudes of oxygen and hydrogen will equal to:

$$\frac{(H_0)_{O_2}}{(H_0)_{H_2}} = \frac{(m)_{O_2}(\partial)_{H_2}(p)_{H_2}}{(m)_{H_2}(\partial)_{O_2}(p)_{O_2}}. \tag{14}$$

We have $m_{O_2} = 16 m_{H_2}$, p is a gas partial pressure and if we are trying to detect oxygen and hydrogen in an air, for partial pressures of that components we will have $p_{O_2} = 2 \cdot 10^4 Pa,\ p_{H_2} = 2 \cdot 10^3 Pa = 0.1 p_{O_2}$. Considering $\partial_{O_2} = \partial_{H_2}$, we will have $\left(H_0\right)_{H_2} / \left(H_0\right)_{O_2} = 100/16 = 6.25$, which means that for same kind of sensor the low frequency magnitude for hydrogen has 6.5 times larger values than for oxygen [see in Fig. (7)]. The curve for oxygen located at the bottom of the curve of hydrogen. Actually in Eq. (14) we have considered that mass, effective area and partial pressure are temperature independent and also assumption that desorption energy is the same for oxygen and hydrogen.

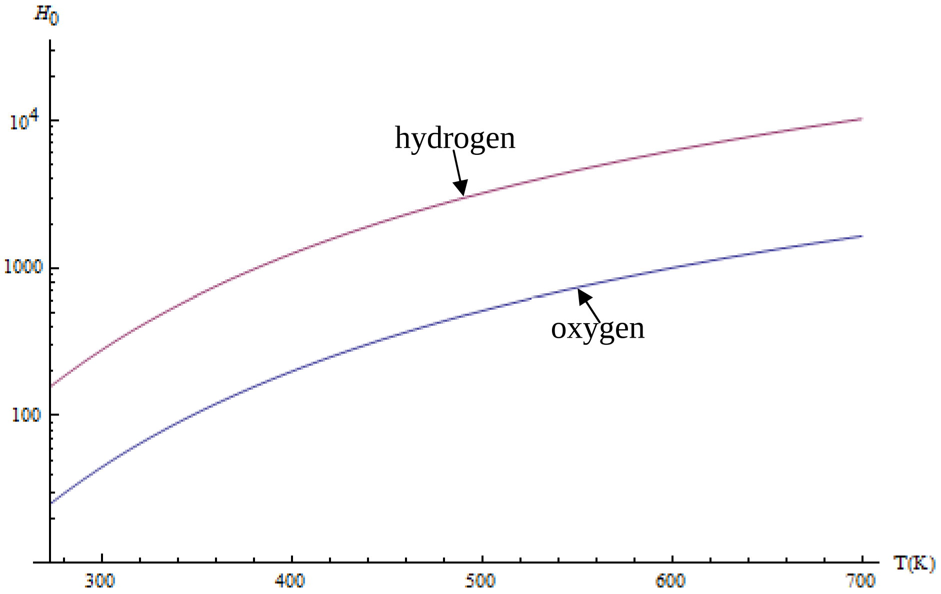

Fig. 7. Temperature dependence of the low frequency magnitude of the PDS of the fluctuation of the free electrons density for oxygen and hydrogen adsorbed on a metal-oxide sensor.

As we already seen at working temperatures $\alpha p >> \beta$ and for Eq. 8 we will have

$$f_c = \frac{1}{2\pi\tau} = \frac{\alpha p + \beta}{2\pi} \approx \frac{\alpha p}{2\pi} = \frac{1}{2\pi}\frac{\aleph \partial p}{\sqrt{2\pi mkT}}. \tag{15}$$

In this case the relationship between corner frequencies of oxygen and hydrogen will equal to:

$$\frac{(f_c)_{O_2}}{(f_c)_{H_2}} = \frac{\sqrt{(m)_{H_2}}\,(\partial)_{O_2}\,(p)_{O_2}}{\sqrt{(m)_{O_2}}\,(\partial)_{H_2}\,(p)_{H_2}}, \tag{16}$$

Putting values of corresponding parameters we will have $(f_c)_{O_2}/(f_c)_{H_2} = 100/4 = 2.5$ which means that values of corner frequency of hydrogen will be 2.5 times lower than values of corner frequency of oxygen. The relationship is shown in Fig. 8.

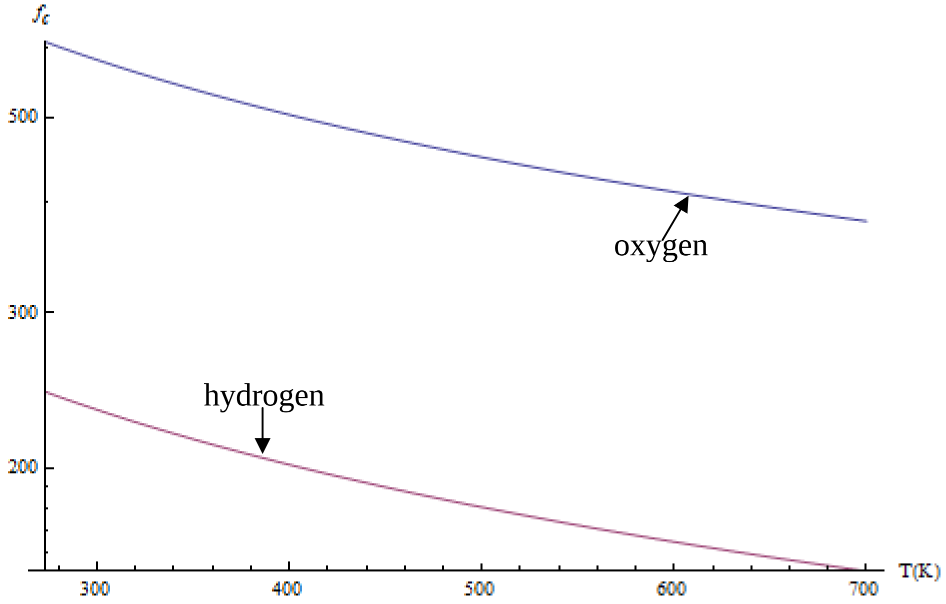

Fig. 8. Temperature dependence of the corner frequency of the PDS of the fluctuation of the free electrons density for oxygen and hydrogen adsorbed on a metal-oxide sensor.

Now we have temperature dependencies of low frequency magnitude and corner frequency dependencies on gas type which means that we can use them to calculate the PDS of free electrons density fluctuation for each kind of gas. As we already seen:

$$S_{\delta G}(f) = \left(e\mu_n \frac{s}{Ld}\right)^2 \frac{H_0}{1+f^2/f_c^2}, \tag{17}$$

$$\frac{(H_0)_{H_2}}{(H_0)_{O_2}} = \frac{100}{16} = 6.25, \frac{(f_c)_{H_2}}{(f_c)_{O_2}} = \frac{4}{10} = 0.4. \tag{18}$$

Using these 2 equations we can plot the figure or PDS of free electrons density fluctuation for oxygen and hydrogen adsorbed on SnO_2 sensor (Fig. 9).

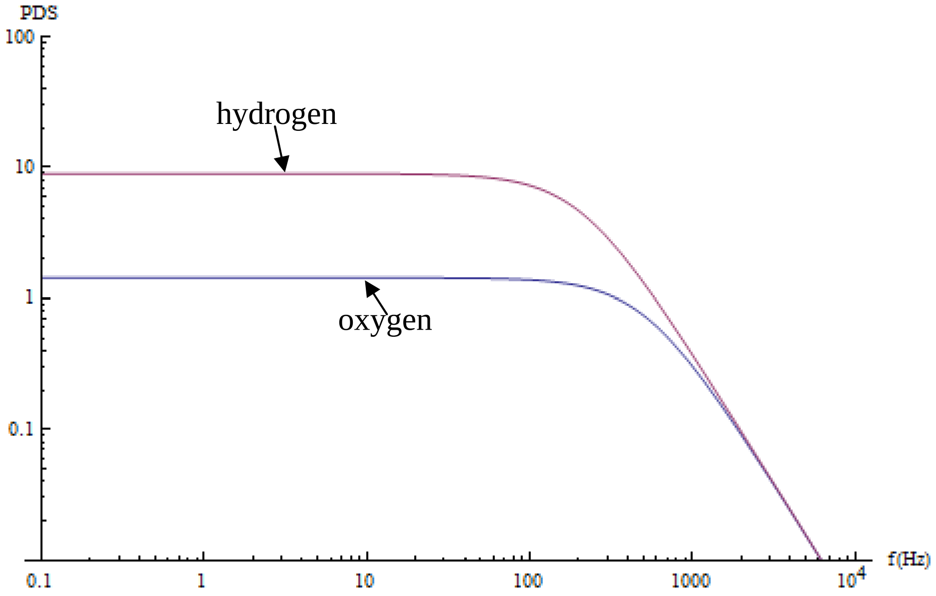

Fig. 9. PDS of the fluctuation of the free electrons density calculated for oxygen adsorbed on the surface of a metaloxide sensor at 373K.

5. Conclusions

Adsorption-desorption Langmuir’s theory for oxygen was extended to other types of gases and considered also the case of reduction in heat of adsorption. Calculations of the low frequency magnitude and corner frequency of Power Density of Spectrum of fluctuation of free electrons density for each case and merging them into formula of PDS were carried out. Powerful method for determination of gas concentration is developed.

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