Application of the carbone nanotube interconnection model for simulation of NH3 gas sensor

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***Abstract*— Nanotubes are a very promising strand for nanoelectronic applications. Among them, in gas sensing. However the modeling of this element depending on the approach makes it difficult to analyze certain behaviors. This work applies a methodology of variation of the total resistance of the nanotube to the gas concentration in an interconnection model of carbon nanotubes with multiple walls. This approach allows to perform electrical schematic tests for simulations and development of other applications, such as a CMOS signal conditioner. For the Specter simulator, the modeled MWCNT showed a correlation above 98% of its curve. sensitivity when compared to a sensor that provided the parameters to estimate the Fermi Energy variation function by the concentration of ammonia.**

I. INTRODUCTION

The carbon nanotubes (CNTs), discovered in 1991, by Sumio [1], are considered an one dimension allotropic form of carbon, since the ratio between its length and diameter is high. Carbon nanotubes are basically divided in two categories: Single-Walled Carbon Nanotubes (SWCNTs), and Multi-Walled Carbon Nanotubes (MWCNTs). The SWCNT can be understood as a ”rolled up” graphene sheet, in cylindrical shape. On the other hand, the MWCNT resemble a group of many concentric SWCNTs with different diameters. While the SWCNTs may be metallic or semiconducting depending on their chirality, giving rise to zigzags (mainly semiconductors), armchairs (metallic) or chiral nanotubes (mainly semiconductors), MWCNTs are always metallic. In addition, MWCNTs have similar current load capacities (such as metallic SWCNTs), but are easier to fabricate than SWCNTs because of easier control of the growth process.

CNTs can find applications in various areas such as flat monitors, absorption and sorting of electromagnetic waves, energy conversion, lithium battery anodes, hydrogen storage, supercapacitors, etc. [2], [3]. In addition to these diverse applications, the CNts are quite promising in the interconnection in VLSI, as they have a long mean free paths (MFPs) in the order of several micrometers (Copper has 40 nm at room temperature), which provide low resistivity and possible ballistic transport on short-term interconnections [4]. And in the absence of damage, a CNT can carry current densities of greater than $10^{10} A/cm^2$ at an elevated temperature of up to 250^oC.

Another promising application of the CNT is as a material for the development of superminiaturized chemical and biological sensors, because high sensitivity of the electronic properties of nanotubes to adsorbed molecules on their surface and the unparalleled unit surface providing such high sensitivity. [5]. The principle of operation of these sensors is based on changes in the V - I curves of the nanotubes as a result of the adsorption of specific molecules on their surface.

This paper aims to present a model of interconnection with multiple-walled carbon nanotubes, already validated in the literature, to develop assays of a nanotube gas sensor. The adjustments discussed in the document focus on the detection of ammonia concentration (NH3).

II. CNT-INTERCONNECT

A reasonable ammount of research have been made to modelling the CNTs interconnections, both single and multi walled, [6]–[9]. SWCNT with semiconductor properties has a higher contact resistance, which limita its application as an interconnection for integrated circuits. On the other hand, MWCNT provide low contact resistance, even smaller than the SWCNT, making them ideal for inteconnection in circuits. [10], [11].

A model used to explain the propagation of eletromagnectic field throughout a CNT is necessary to study the efficiency of a CNT interconnection. In literature, it is possible to summarize three theories as the basis of the construction of different models. The first model is based in concepts of quantum dynamics and the liquid theory of Lüttinger [12]; the second model was constructed from the Boltzmann's Transport Equation (BTE) [13]; and at last, Maffuci et al. [14] researched the transportion of electrons along a CNT and proposed the third model, the fluid model. The fluid model was developed in scope of CNT-based circuit modelling, with classical electrodynamics, and it is simple in concepts and mathematical modelling.

A. CNT-Interconnect Model

The compact model of the MWCNT used is proposed by [9], and originates from the compact model developed by [8], based on the fluid model. Except the contact resistance R_{CON} and the resistance induced by defects R_{Def}, all parameters are calculated similarly to those in [8]

The number of walleds to a MWCNT is calculated from (1) and (2). The p variable reffers to the number of CNT walleds (shells). The D_{CNTmax} represents the outter diameter of the MWCNT; d is the Van der Waals (0.34nm).

$$p = 1 + \text{Inter}\left[\frac{(D_{CNT_{\max}} - D_{CNT_{\max}}/2)}{2d}\right] \tag{1}$$

where $Inter[...]$ signals that only the integer part is considered in the interaction of the terms on the left in Equation (1). Counting from the outter to inner shells as 1, 2, . . ., i, . . ., and p, then D_{CNTi} is the diameter of the i^{th} shell, in the MWCNT.

$$D_{CNT_i} = D_{CNT_{\max}} - 2d(i-1), 1 \leq i \leq p \tag{2}$$

A shell resistance is composed by three elements [8]: quantum contact resistance R_Q, spreading resistance R_S and imperfect contact resistance R_{mc}. The R_Q and R_S are intrinsics, and R_{mc} is related to the fabrication process. The value of the intrinsic resistance R_i is determined by (3).

$$R_i = R_Q + R_{S_i}L = \frac{h}{2e^2 N_{C_i}} + \frac{h}{2e^2 N_{C_i}}\frac{L}{\lambda_i} \tag{3}$$

$$\lambda_i \approx 1000 D_{CNT_i} \tag{4}$$

where N_{Ci} and λ_i are respectively, the number of conducting channels and the mean free path (MFP) of the shell i. L is the lenght of the CNT shell. The imperfect contact resistance R_{mc} can vary from zero to hundreds of kΩ to different growth processes. As shown in [15], the R_{mc} in a MWCNT can be very small in comparison to the total resistance.

[16] shows that defects induce a resistance R_{DEFi} (Ω) in metalic CNTs, which is proporcional to the density of defects N_{Defi} (nm^{-1}) and inversily proportional to the shell diameter D_{CNTi} ($\mathring{A}$), on (5), where L is the lenght of the CNT shell.

$$R_{DEF}(N_{Def_i}, D_{CNT_i})_i = 2.67 \times 10^5 \times N_{Def_i} \times L \times D_{CNT_i}^{-1.27} \tag{5}$$

$$R_{CON_i} = 1.8514 A_i^{-1} + 1.4685(\text{k}\Omega), A_i = \frac{\pi D_{CNT_i}^2}{4} \tag{6}$$

According to [9] the contact resistance of Pd-CNT for each shell can be obtained as shown (6):

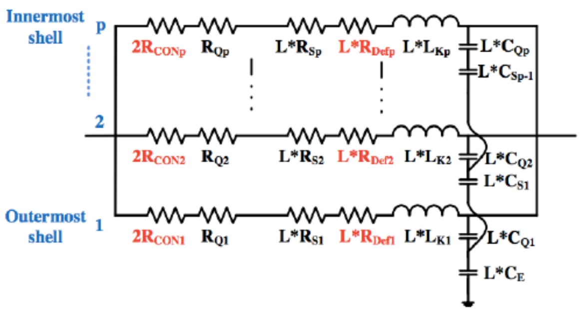

Fig. 1. Concentrated Compact Model

From the *distributed compact model* of [8], a *concentrated compact model* is developed as shown in Fig. 2. The concentrated parameters are calculated by the multiplication of the distributed parameters by the length of the MWCNT. [9] shows that the concetrated compact model is precise and much more efficient than the distributed compact model.

III. Gas Sensors from carbon nanotubes

The carbon nanotubes have all their weight concentrated on the surface of its walleds, what causes a large unit surface, which in turn defines the electrochemical adsorption properties of the nanotubes. The extremely high adsorption capacity of the CNT and the excelent sensibility of the CNT properties to adsorbed atoms and molecules on its surface [17] enables the design of gas sensors based on nanotubes [18], [19]. Currently, various types of gas detectors based on CNT are discussed on literature [17]. The sensors can be classified by the type of variable to be considered in the sensing process the CNT, as listed below:

1) sorption gas sensors;
2) ionization gas sensors;
3) capacitance gas sensors;
4) resonance frequency shift gas sensors.

A. Sorption gas sensors

The adsorption gas sensors are presented in greater quantity than the other types of gas sensors [20]. Its principle of operation is focused on the adsorption, during which an adsorbed gas molecule interacts with a carbon nanotube and tranfers or removes from it, an electron. That modifies the electrical properties of the CNT, and that can be detected. There are gas sensors based on pure CNT, both for single or multi walled, as well those based in CNT modified by functional groups, polymers, metal doping, or metal oxides.

As presented in the works of [21], [22], the single walled CNT is sensible to gases such as NO2, NH3 and some volatile organic compounds due the alteration of the nanotubes conductivity conductivity as a result of the adsorption of the gas molecule in its surface. [23] have developed sensors for the detection of gaseous molecules of ammonia by chemical vapor deposition (CVD). In this study, they showed the reduction of MWCNT resistance in the presence of the gas. In the work [24] the process of creating the sensor was similar to [23], however the MWCNT was deposited in on Pt patterns of alumina. In the work of [25] the electrodes were Au. In these three studies, ammonia exposure occurred at room temperature, 27^{o}C

B. NH3 gas sensor of carbon nanotube model

In order so the interconnection CNT model proposed by [8] and [9] can be used to trials of gas sensors it is necessary that the concentration of a gas be a variable in the calculation.

In this section it is presented a analytical method of calculation of the gas concetration impact on the number of conducting channels N_C by means of the displacement on the Fermi level E_f. As shown in [26], the MWCNT when exposed to NH3, its level of conductance changes.

The band structure of a CNT can be described by (7) [27], where D_{CNT} is the diameter of the CNT, k_x is the wave vector on the direction x, t is the jump parameter, a_0 is the distance carbon-carbon, and v is the integer number below m (that can be calculated from D_{CNT} [27]).

$$E(k_x) = \pm\frac{3ta_0}{2}\sqrt{k_x^2 + \left(\frac{1}{D_{CNT}}(2v - \frac{4}{3}m)\right)^2} \quad (7)$$

Since the band structure is parabolic near the points k = 0, $E(k_x)$ can be described as:

$$E(k_x) \approx \pm\frac{E_g}{2} + \frac{h^2k_x^2}{2m} \quad (8)$$

where h is the reduced Plank constant, m is the effective mass of the CNT that depends on the tube diameter [[28], [29]].

We can calculate the transmission coefficients $(T(E))$ to obtain the number of conducting channels N_C from (8). Equation (9) shows this calculation. [9].

$$N_C = \int T(E)f'(E, E_f)dE/(k_BT) \quad (9)$$

In the literature, MWCNTs applied in the sensing of ammonia gas are found in the works of [23], [24] and [25]. The response of the sensors are contained in Fig. 2. The sensitivity is defined in (10), where R_0 is the initial resistance without presence of NH3.

$$\Delta S = \frac{(R - R_0)}{R_0} \quad (10)$$

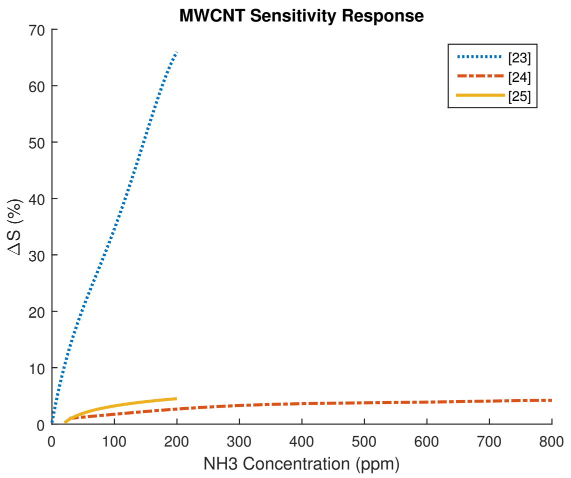

Fig. 2. Resistive sensitivity of the gas sensor to the MWCNT of [23], [24], [25].

The variable E_f had its value changed in the interconnection model, which the resistance value for each measure was estimated. The MWCNT constructive parameters for all the tests performed are presented in Table 1. The result of the variation of E_f is in Fig. 3. In Fig. 4 we have the sensitivity found for variation of E_f, applying (10).

TABLE I
DATA USED IN THE MWCNT INTERCONNECTION MODEL

Name	Description	Value
L	Length of MWCNT (m)	1E-6
Def	Defect density (/nm)	0
Dmax	Outermost diameter of the MWCNT (m)	4E-9

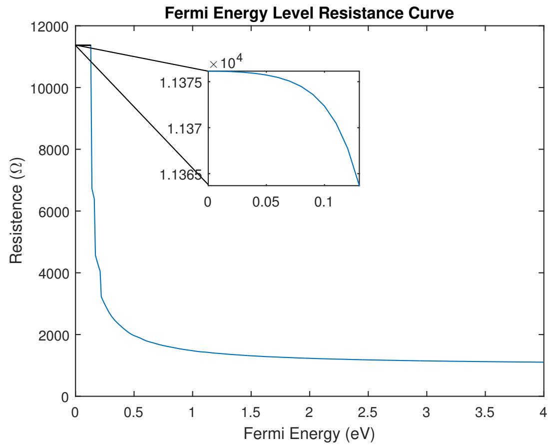

Fig. 3. Resistance curve by the Fermi Energy variation in the interconnection model

We can compare the results obtained in Fig. (3) and Fig. (4)it is possible to note certain similarities between zones of the curve in Fig.3 with the responses of the jobs of [23], [24] and [25] .

After this preliminary analysis, it knowing that the gas concentration affects the Fermi energy level and these change the resistance value, we define (11) e (12), as the sensitivity function (ΔS_i) per gas concentration (F) from [23], [24] and [25] and the sensitivity function (ΔS_{CNT}) of the model by E_f, respectively.

$$G : F \mapsto \Delta S_i \Leftrightarrow \Delta S_i = G(F) \quad (11)$$

$$H : E_f \mapsto \Delta S_{CNT} \Leftrightarrow \Delta S_{CNT} = H(E_f) \quad (12)$$

What is wanted at the moment is to find among the sensors selected in the literature a function $(K(x))$ that relates the variation of concentration of NH3 with the Fermi Energy, taking into account the variation of this with the sensitivity of the model in relation to sensor sensitivity in the literature. For this step, we first determine in (13) a function I_i that relates the sensitivities.

$$I : \Delta S_i \mapsto \Delta S_{CNT} \quad (13)$$

After this, the left compound is performed in the functions, which having as condition that the functions are injectors. In (14) the existence of the $K(x)$ function is assumed.

$$H \circ K \circ G^{-1} : \Delta S_i \mapsto \Delta S_{CNT} \quad (14)$$

We apply (13) to (14)

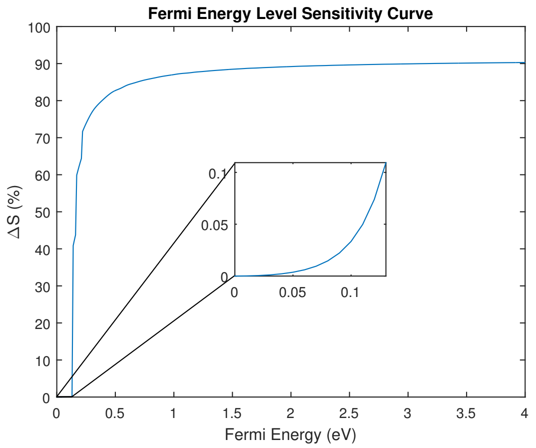

Fig. 4. MWCNT sensitivity curve for Fermi Energy variation in the interconnection model.

$$K \circ G^{-1} = H^{-1} \circ I \tag{15}$$

Finally, we leave the function $K(x)$ evident in (ref eq: k) we arrive at the desired relation.

$$K = H^{-1} \circ I \circ G \Rightarrow H^{-1} \circ I \circ G : F \mapsto E_f \Leftrightarrow E_f = K(F) \tag{16}$$

With the steps of (13) a (16), we obtain for each case the model response for gas concentration. It should be noted that one of the prerequisites for obtaining the process in (15) is that the functions are injectors, which does not occur in case [24] and [25]. However, if the gas concentration range is restricted, within that range the function will have its behavior similar to an injection function.

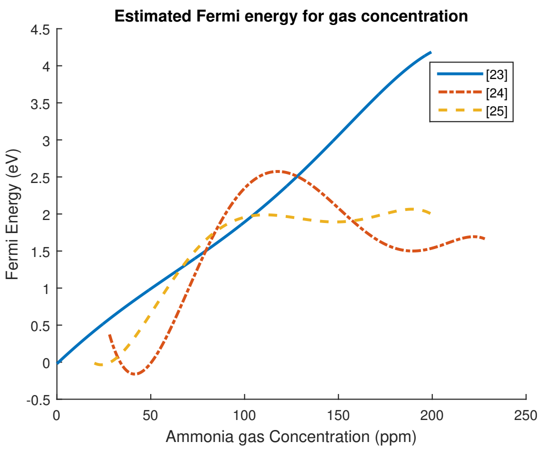

Fig. 5. Curves obtained for variation of the Fermi Energy by the variation of the gas concentration.

Several factors were left aside to obtain the results, as the influence of the temperature, since all the works used did the tests with room temperature (27ºC). As well as the time of exposure of the sensor to the gas, which differed in each study and the type of contact in the terminals deposited the MWCNT. These unweighted factors allow us to consider the cause of the difference between the curves obtained.

IV. Simulation of the Interconnection Model Applied to Gas Sensor

To perform tests of the MWCNT as gas sensor, the code in VerilogA was implemented in Cadence Virtuoso software and Specter simulator

For tests, only the regression from [23] was simulated. In Fig. 5 has the behavior of the resistance in the MWCNT to vary the concentration of ammonia.

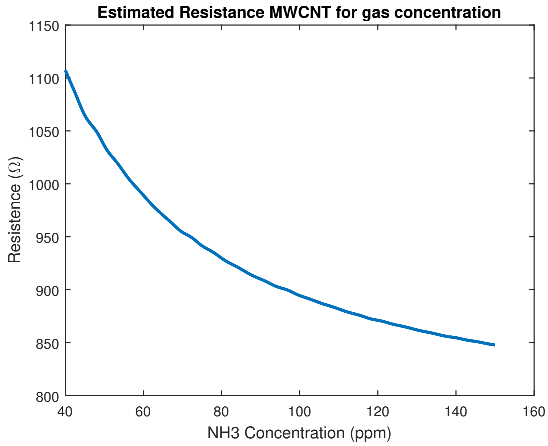

Fig. 6. Estimated resistance curve of the interconnection model for varying the gas concentration

For the tests, the simulator limited the variation of the NH3 concentration from 40 to 150 ppm. The cause was convergence in the simulation, coming from the approximation that occurs in the model for values of E_f below $0.8eV$. After the analysis of the resistance of the model in Fig. 6, a comparison was made between the sensitivity curves of the modified interconnection model with that of [23], as shown in Fig. 7.

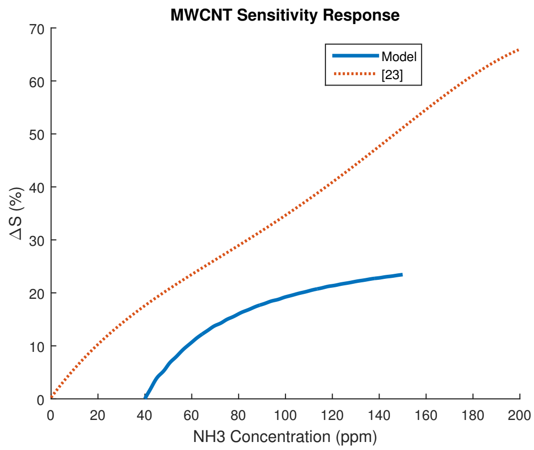

Fig. 7. Resistive sensitivity of the gas sensor to the MWCNT of [23] and interconnect model

It is possible to note in Fig. 7 that in the interval between 40 and 75 ppm, the behavior of the model and sensor

[23] is quite similar, with a correlation between curves of approximately 0.9307. However, for concentrations above 75 ppm, the sensitivity of the model is more pronounced. The hypothesis raised for such a difference is the contact resistance in MWCNT, which work [23] did not provide, whereas that of the model was estimated by [9].

V. CONCLUSIONS

The CNT tests are more practical with the fluid model proposed by [8] and modified by [9]. However, for the Fermi Energy values smaller than $0.8eV$, a convergence error occurs in CADENCE simulator Sprectre. In preliminary analyzes the cause is in the approach of the floating point of the values in the simulator.

The estimation of the Fermi energy variation to be applied in the interconnection model was shown to be feasible with the use of sensors in the literature. However, due to variables not considered, for example, exposure time of the MWCNT to the gas, discrepancies occurred. For further validation, direct data from a sensor to MWCNT is required. The sensitivity of the patterned sensor when compared to the sensor [23] had a correlation rate greater than 90% in the range of 40 to 75 ppm.

ACKNOWLEDGMENT

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - (CAPES) - Finance Code 001.

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