"Modeling Memristive Biosensors"

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Abstract—In the present work, a computational study is carried out investigating the relationship between the biosensing and the electrical characteristics of two-terminal Schottky-barrier silicon nanowire devices. The model suggested successfully reproduces computationally the experimentally obtained electrical behavior of the devices prior to and after the surface bio-modification. Throughout modeling and simulations, it is confirmed that the nanofabricated devices present electrical behavior fully equivalent to that of a memristor device, according to literature. Furthermore, the model introduced successfully reproduces computationally the voltage gap appearing in the current to voltage characteristics for nanowire devices with biomodified surface. Overall, the present study confirms the implication of the memristive effect for bio sensing applications, therefore demonstrating the Memristive Biosensors.

Keywords—Biosensor; Memristor; Silicon nanowire; Schottky barrier;

I. INTRODUCTION

Memristor, the fourth fundamental circuit element was first presented by Leon Chua in 1971 [1]. The most basic mathematical definition of a memristor is that of a current-controlled device for circuit analysis that is characterized by its memristance and provides a functional relation between charge and flux. In the case of linear elements, memristance is a constant and thus identical to resistance. In the case where memristance is a function of charge yields a nonlinear circuit element, acting like a resistance with a memory and giving a frequency-dependent Lissajous figure as electrical response to a sinusoidal input, one of the most important properties of the memristive systems and a signature of each memristor. Therefore memristor is a special member of non-linear dynamic systems named memristive systems [1]-[3].

In 2008 the memristor aspect was refreshed by HP Labs researchers, presented a physical model of memristor, connecting the mathematics of the existing theoretical aspect and the physical properties of practical system [4]. The suggested study successfully realizes a nano-scale electronic component, exhibiting physical properties that can be perfectly explained by the memristor theory. The structure proposed and studied is a physical model, so-called Drift model and can be considered as simple analytical example, that memristance arises naturally in nanoscale systems in which solid-state electronic and ionic transport are coupled under an external bias voltage.

In 2011 Leon Chua published a work arguing that all twoterminal non-volatile memory devices based on resistance switching are memristors, regardless of the device material and physical operating mechanisms [3] opening new perspectives in memristive behavior study and new possibilities for applications including memristive systems. Therefore it is suggested that the current to voltage characteristics of some devices and systems, can be modelled using the memristor theoretical aspect.

Memristive devices have already been used in many applications especially in the fields of logic design and memory issues, since memristors enable new possibilities for computation and non-volatile memory storage. Indicatively, memristors are explored for their potential use in dense programmable logic circuits [5] and also applications concerning artificial synapses [6],[7] and cellular nonlinear networks (CNNs) [8] have been suggested. Moreover, it is worth mentioning the introduction of the Resistive RAM (ReRAM) memories [9],[10] which can be classified as memristors and are suitable candidates for standalone memory applications and Generic Memristive Structure (GMS) [11] for 3-D FPGA applications for steering logic, capable in replacing the traditional pass-gates in FPGAs.

Among the different applications that memristive effect had already been introduced, a further approach leveraging the memristive behavior of nanofabricated wires has been suggested and applied for biosensing purposes [12],[13]. Experimentally obtained electrical characteristics of twoterminal Schottky-barrier silicon nanowire devices exhibit hysteretic properties and hysteresis loop at zero voltage. The memristive silicon nanowires are fabricated through a topdown fabrication process, using commercially available (100) oriented Silicon-On-Insulator wafer. The nanowires are defined using electron beam lithography, etched trough a Bosch process of crystalline silicon and anchored between two NiSi junctions that consist the contacts for electrical characterization In order to obtain the memristive biosensors, the devices are functionalized by exposing the surface to GPTS solution and then antibody attachment follows on the devices surface. When biological substances are present on the devices' surface the hysteresis appears shifted to different voltage values, leading to a label-free bio-detection method. In the present work a computational study is carried out aiming at the design of a model that reproduces and emulates the behavior of the physical system prior to and after the bio-modification of the nanofabricated devices. The model aims to be a link between the theory concerning the memristors and the experimental aspect, opening new perspectives for biosensing applications.

II. MATERIALS AND METHODS

A. Computational Methodology

A memristor macromodel is designed and created, as inspired by A. Rak et al. [14] and Z. Biolek et al. [15],[16]. The macromodeling of the memristor is based on the theoretical memristor introduced by L. Chua [1]-[3] and S. Williams [4] and is realized by using CADENCE (R) OrCAD Capture and Capture CIS software. A SPICE source code for the macromodel of the memristor is imported and included in the software's library. The memristor element is designed and introduced in the CADENCE (R) electronic design software and then attached to the created memristor library. Equivalent circuits are then introduced consisting of the memristor macromodel that is considered as reference point in combination to analog circuit elements targeting at emulating the behavior of the physical system and studying the resulting electrical characteristics.

B. Computational Electrical Characteristics

Simulations are implemented under a sinusoidal input voltage selected to match the experimental set up input values. The current to voltage results obtained by the simulations in Fig.1 depict the characteristic pinched hysteresis loop at zero voltage validating qualitatively and quantitatively the functionality of the model and confirming the fact that the model actually describes the operation of a memristor according to theory [1]-[3]. The effect of the different frequencies in the current to voltage characteristics is also studied. Varying the input voltage frequency does not affect the memristive behavior but it modifies the shape of the memristive curve accordingly to previous literature [1]-[3], [4]. The memristive effect diminishes as the frequency is increasing and the characteristics become closer to linear. Simulations are carried out for different frequencies values and confirm this behavior. In order to make clear the impact of the frequency to the current to voltage characteristics, the results for the frequency values of 300Hz and 1000Hz are reported in Fig.1.

In order to draw conclusions regarding the experimental results concerning the presence of biological substances on the nanowire surface, semi-logarithmic range for the current with respect to input voltage curve is of the most significant interest. The corresponding semi-logarithmic current to voltage curve for the pure memristor model is presented in Fig. 2 and as expected both the two local minima for the forward and the backward regimes occur for zero input voltage.

III. RESULTS AND DISCUSSION

For simulating the electrical response of the bare silicon nanowire devices under study, an equivalent circuit model is

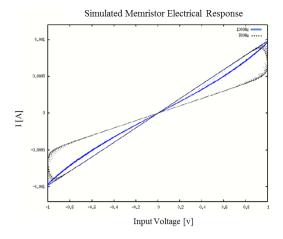


Fig. 1. Frequency dependence computantional electrical characteristics. Frequencies of 300Hz (black dotted line) and 1000Hz (blue line) and voltage amplitude of 1Volt.

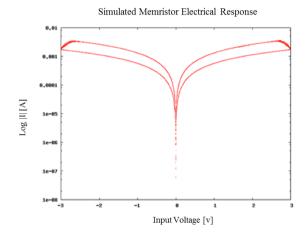


Fig. 2. Computational semi-logarithmic current to voltage characteristic curve obtained from simulating the pure-memristive behavior. The simulation voltage amplitude applied is 3Volts and the frequency 700Hz.

developed in Fig.3, taking inspiration from the concept that is introduced by Elhadidy et al. [17] but consisting of a memristor sandwiched between two identical head-to-head Schottky barriers. The Schottky barriers are represented by sub-circuits consisting of a diode in parallel to a resistor and result to a slight modification of the memristive curve.

More specifically, the introduction of a diode to the initial system brings to the memristive curve the typical Schottky contact shape at the branches of the characteristic semilogarithmic current to voltage curve without affecting the location of the current minima.

A unique current corresponds to each applied voltage. If the polarity of the bias voltage is exchanged, the reverse-biased barrier would be exchanged with the forward-biased one and vice versa. In addition, experimental current to voltage characteristics present noticeable asymmetry at the branches of the semi-logarithmic current to voltage characteristics.

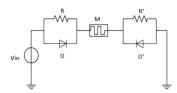


Fig. 3. Equivalent circuit modeling the nanofabricated device prior to the bio-modification.

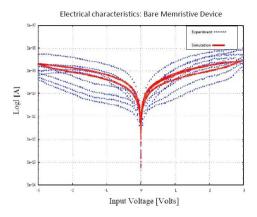


Fig. 4. Semi-logarithmic current to voltage simulation results (red curve) obtained from the equivalent circuit (Fig.3) comparing the experimental results from the electrical characterization of a bare nanofabricated device (blue dotted curves). The current minima for forward and backward regimes occur for zero voltage.

The concept of the non-identical Schottky barriers is taken into consideration in the equivalent electrical circuit through R' in combination to the fact that during the one circle of the current (depending on the polarity of the bias voltage) the one diode does not conduct due to the forward and reverse bias nature of the diode and consequently only the remaining resistivity origin from the reversed bias Schottky diode finally contributes. Simulation results obtained by the aforementioned equivalent circuit are compared to experimental data and presented in Fig. 4. The nanofabricated devices usually present a non-identical behavior by nature. It is demonstrated that the simulation curve follows in good approximation the average behavior of the physical system. According to this, it can be concluded that the experimental results present a current to voltage characteristic curve equivalent to that of a memristor device electrically contacted by two asymmetric Schottky barriers, validating the hypothesis that the experimental set up deals with memristive behavior.

The most innovative change introduced by the biofunctionalization is the difference in the bias voltage used for reaching current minima. Namely, a voltage gap is created after the functionalization with biological molecules as a further memory effect on the voltage scan across the nanowire [12],[13]. A Schottky diode can also be described with an equivalent circuit model consisting of a non-linear capacitor in parallel to a non-linear resistor accordingly to literature [18]. The capacitor stands for the space charge capacitance and reflects only the free carriers of the material, while the resistor represents the residual conductance of the diode.

An equivalent circuit containing non-linear sub-circuits (RC) consisting of a non-linear capacitor in parallel to a nonlinear resistor is further then introduced in Fig.5 in order to model the presence of the voltage gap, after the biomodification of the nanofabricated device. It is demonstrated in Fig.6 that the two current minima are clearly separated and a voltage gap appears in the semi-logarithmic current to voltage characteristics as due to the presence of the capacitors now introduced giving successful fitting with the experimental data. According to the literature concerning measurements of the junction capacitance [18]-[21] values for the space charge capacitance are referred to belong in the range beginning of pF [18],[19] and reaching the values of nF [20],[21]. Furthermore, it is mentioned that the excess capacitance is a result of the combination in parallel of the space charge capacitance characterizing the diode and of the diffusion capacitances due to the minority carriers' injection. The reported values concerning the excess capacitance reach 43nF and it is considered that the excess capacitance mainly originates from the bulk silicon rather than the interface of the diode in study [21] while typical capacitance values concerning only contributions by the depletion area are in the range of pF [18],[19]. The values for the equivalent capacitance introduced for achieving successful fitting with the experimental data are in the range of the values reported in literature concerning the excess capacitance and thus, it is demonstrated that the presence of biomolecules on the device interacts deeply with the conductivity of the channel related to minority carriers.

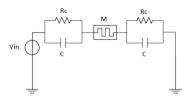


Fig. 5. Equivalent circuit modeling the nanofabricated device after the biomodification.

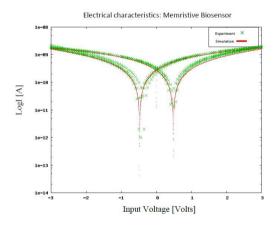


Fig. 6. Semi-logarithmic current to voltage simulation results (red curve) obtained from the equivalent circuit (Fig.5) comparing to experimental results from the electrical characterization of a bio-modified nanofabricated device (green dotted curves). The two current minima for forward and backward regime are clearly separated and a voltage gap can be clearly observed.

IV. CONCLUSIONS

In this paper, a computational study is carried out targeting at the investigation of the electrical characteristics obtained from freestanding two-terminal memristive biosensors. The experimental data indicates that the current to voltage characteristics corresponding to the bare nanofabricated devices present hysteretic loop at zero voltage. However, when biological substances are present on the device surface, the hysteresis shows a voltage gap in the semi-logarithmic current to voltage curve.

A macromodel of a memristor element is created and combined with analog circuit elements forming equivalent circuit models in order to reproduce and emulate the behavior of the physical system. In addition, the simulation outcomes demonstrate the dependence of the system's electrical behavior from the input voltage parameters.

The results obtained through simulation present successful fitting with the experimental results for bare devices and for devices with bio-modified surface offering a bridge between the experimental electrical characteristics from the nanofabricated wires and the theoretical aspect of memristive theory. For the case of bare two-terminal Schottky-barrier silicon nanowire devices the simulation curve follows in good approximation the average behavior of the physical system and it can be concluded that the experimental results present electrical behavior equivalent to that of a memristor device electrically contacted by two asymmetric Schottky barriers, validating the hypothesis that the experimental set up deals with memristive behavior. Moreover, the voltage gap presented in the electrical characteristics of the devices after the bio-modification with biological substances is also successfully computationally simulated and it is related to capacitive effects due to the minority carrier in the nanowire device.

Overall, the computational study presented in the current work offers an extremely good link between the concepts of analog electronics and biosensing and confirms the potential of memristive effect for biodetection applications.

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REFERENCES

- [1] L. Chua, "Memristor-The missing circuit element", IEEE Trans. Circuit Theory, 18(5):507 519, 1971
- [2] L. Chua, S. Kang, "Memristive devices and systems", Proc. IEEE, 64(2):209–223, 1976

- [3] L. Chua, "Resistance switching memories are memristors", Appl. Phys. A, 102(4):765-783, 2011
- [4] D. Strukov, G. Snider, D. Stewart, S.Williams, "The missing memristor found", Nature, 453:80-83, 2008
- [5] G. Rose, J. Rajendran, H. Manem, R. Karri, and R. Pino, "Leveraging Memristive Systems in the Construction of Digital Logic Circuits", Proc. IEEE, 100(6):2033-2049, 2012
- [6] R. Waser and M. Aono, "Nanoionics-based resistive switching memories", Nature Materials, 6: 833 – 840, 2007
- [7] Y. Pershin and M. D. Ventra, "Experimental demonstration of associative memory with memristive neural networks", Neural Netw. 23 (7):881-886, 2010
- [8] E. Lehtonen and M. Laiho, "Arithmetic Operation within Memristor-based Memory", 12th International Workshop on Cellular Nanoscale Networks and their Application (CNNA 2010), Berkeley, CA, pp. 1-4, 2010
- [9] D. Sacchetto, P.E. Gaillardon, M. Zervas, S. Carrara, G. De Micheli and Y. Leblebici, "Applications of Multi-Terminal Memristive Devices", IEEE Circuits and Systems, 13(2):23-41, 2013
- [10] D. Sacchetto, H. Ben-Jamaa, S. Carrara, G. De Micheli, and Y. Leblebici, "Memristive Devices Fabricated with Silicon Nanowire Schottky Barrier Transistors", in Proceedings of the IEEE International Symposium on Circuits and Systems (ISCAS 2010), Paris, France, vol. 1, pp. 9-12, 2010
- [11] P.-E. Gaillardon, D. Sacchetto, S. Bobba, Y. Leblebici and G. De Micheli. "GMS: Generic Memristive Structure for Non-Volatile FPGAs", IFIP/IEEE International Conference on Very Large Scale Integration (VLSI-SoC), Santa Cruz, California, USA, pp. 94–98, 2012
- [12] D. Sacchetto, M.A. Doucey, G. De Micheli, Y. Leblebici and S. Carrara, "New Insight on Biosensing by Nano-fabricated Memristors", BioNanoSci. 1:1–3, 2011
- [13] S. Carrara, D. Sacchetto, M.A. Doucey, C. Baj-Rossi, G. De Micheli and Y. Leblebici, "Applications of Multi-Terminal Memristive Devices: A Review", Sensor Actuat. B-Chem. 171-172: 449-457, 2012
- [14] A. Rak, G. Cserey, "Macromodeling of the Memristor in SPICE", IEEE Trans. Computer- Aided Design Integr. Circuits Syst. 29(4):632 – 636, 2010
- [15] Z. Biolek, D. Biolek, V. Biolkova, "SPICE model of memristor with nonlinear dopant drift", Radioengineering, 18(2):210–214, 2009
- [16] Z. Biolek, D. Biolek, V. Biolkova, "Pinched hysteretic loops of ideal memristors, memcapacitors and meminductors must be selfcrossing", Electron Lett. 47(25):1385-1387, 2011
- [17] H. Elhadidy, J. Sikula, J. Franc, "Symmetrical current-voltage characteristic of a metal- semiconductor-metal structure of Schottky contacts and parameter retrieval of a CdTe structure", Semicond.Sci.Technol. 27(1):015006, 2012
- [18] K. Steiner, "Capacitance-voltage measurements on Schottky diodes with poor ohmic contacts", IEEE Trans. Instrum. Meas. 42(1):39–43, 1993
- [19] M. Bleicher, E. Lange, "Schottky-barrier capacitance measurements for deep level impurity determination", Solid State Electron. 16(3) :375-380, 1973
- [20] P. Ho, E. Yang, H. Evans, X. Wu, "Electronic states at silicide-silicon interfaces", Phys. Rev.Lett. 56(2):177-180, 1986
- [21] J. Werner, A.-F.-J. Levi, R.-T. Tung, M.Anzlowar, M. Pinto, "Origin of the excess capacitance at intimate Schottky contacts", Phys.Rev. Lett. 60(1):53-56, 1988