Reliable Gas Sensing with Memristive Array

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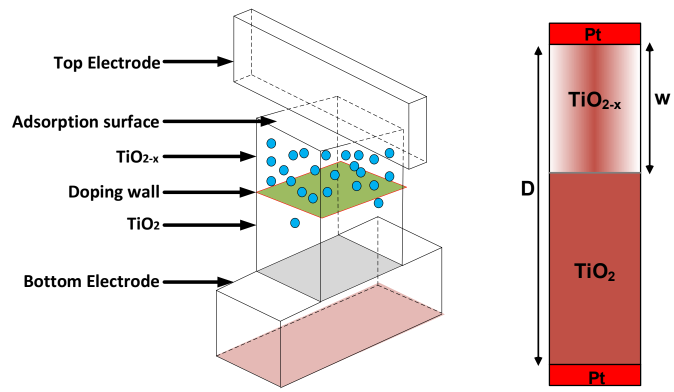
***Abstract*—Gas sensing is one of the proposed application field of memristive devices. We used a crossbar array of memristors as gas sensor using the HP labs fabricated TiO_2 based memristor model in an attempt to improve sensing accuracy. We introduced the possibility of reliable multiple gases detection using multiple rows of memristors as separate sensor in a crossbar array. Our experimental results show that an array of memristors can minimise measurement errors as well as provide a good redundancy measure during gas sensing. Measurements taken from the sensors are also not affected by alternate current paths problem often experienced in crossbar architecture.**

***Index Terms*—Memristor, gas sensor array, memory, crossbar array, metal oxide.**

I. Introduction

The use of metal oxide nanoscale devices as gas sensors and biosensors has grown in recent years [1]. Some common metal oxide semiconductors sensor include tin oxide (SnO_2), zinc oxide (ZnO), chromium titanate (CTO) among many others. With respect to other sensor technologies they are simple, inexpensive, miniaturizable and of good responsitivity [2].

TiO_2 metal oxide semiconductor, which form the crux of this paper was used by HP Labs to fabricate the first physical memristor device [3]. Generally, when semiconducting metal oxide are used as gas sensor, the main cause of change of the sensor's resistance is due to the loss (gain) of free charge carriers (electrons or holes) from (to) the semiconductor to (from) its surface [4]. The initial and final resistances of the device after gas exposure are measured and the properties of such gas are determined from the measured values. Gas sensing with single device could be prone to measurement and reliability issues due to environmental and/or variation in the device itself. These issues could be reduced statistically by taking multiple measurements from the same sensor or from different independent sensors [5]. This paper explores the use of memristor as sensor in crossbar architecture with emphasis on the sensor's response to gas presence. A structural analysis of memristive sensor array such as the one introduced in this paper could be used in the early stages of new smart sensing system development, to simulate the overall behavior and in identifying any vulnerabilities before any actual system is developed. In terms of memristor model used for analysis in this work, any of the existing memristor model can be adapted for the purpose of simulating gas sensor as long as the model is based on a gas sensitive metal oxide semiconductor. TiO_2 based memristor was used for all analysis in this work.



(a) (b)

Fig. 1. (a) Structure of memristor for sensing applications. Both sides of the top contact is left uncovered to enhance interaction of target gas with the titanium oxide layer (b) Structure of the TiO_2 based memristor fabricated by HP Labs.

The rest of the paper is organized as follows. Section II introduces metal oxide memristor's application in gas sensing. Section III describes the proposed multiple gases sensing structure using crossbar array and section IV concludes the paper.

II. Memristor as a Gas Sensor

In order for a memristor to be effective as a gas sensor, a slight modification will be incorporated into devices fabricated for sensing purpose. The physical memristor will feature a partially covered top terminal as shown in Fig. 1a to allow gas interaction with the semiconductor layer. The exposed part of the TiO_{2-x} with resistance value of R_{on} allows for easy interaction between the gas and the surface of the memristor via both sides of the top contact. The pure TiO_2 with resistance value of R_{off} is assumed to be unaffected by the gas directly [6]. The value of R_{on} changes to R_{on_eff} using the adaptable response model equation in Eqn. 1 [7], [8] depending on the type of gas interacting with the memristor.

$$S = \frac{R_{init}}{R_{final}} = 1 + A[C]^{\beta} \tag{1}$$

The response equation above is computed based on the concentration C of the target gas, A is the constant parameter or response coefficient for the material of the semiconductor and β is the response order for the subject gas. R_{init} and

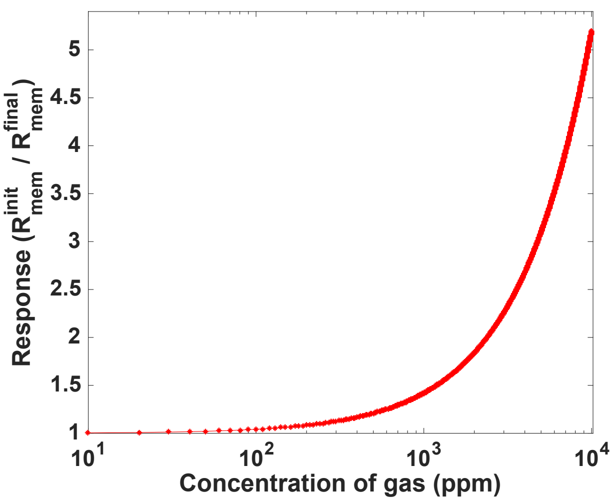


Fig. 2. Sensor response to different concentrations of an oxidising gas. R_{mem}^{init} is calculated using Eqn. 2 with the initial values of R_{on} R_{off}. R_{mem}^{final} (Eqn. 3) is the memristance of the sensor after gas interaction, where R_{on} changes to $R_{on_{eff}}$.

R_{final} are the initial and final resistance values of the sensor respectively. Therefore, for any oxidising gas of concentration C, the response of a gas sensor made of p-type semiconductor can be represented directly by Eqn. 1. Clearly, the response of a p-type material to a reducing gas can also be represented by the inverse of Eqn 1. In summary, the total resistance of the memristor is determined by two resistors R_{off} and R_{on} representing the resistance of the undoped (TiO_2) and the doped (TiO_{2-x}) regions (Fig. 1b) of the memristor respectively. TiO_{2-x} is p-type semiconductor and its resistivity (R_{on}) decreases (increases) in the presence of an oxidising (reducing) gas.

The model thus uses the new R_{on_eff} and R_{off} to compute the final memristance (R_{mem}^{final}) of the device after exposure to the target gas using Eqn. 3. The initial memristance of the device is calculated with R_{on} as in Eqn. 2.

$$R_{mem}^{init} = R_{on}\frac{w(t)}{D} + R_{off}\left(1 - \frac{w(t)}{D}\right) \tag{2}$$

$$R_{mem}^{final} = R_{on\_eff}\frac{w(t)}{D} + R_{off}\left(1 - \frac{w(t)}{D}\right) \tag{3}$$

where $w(t)$: $0 \leq w(t) \leq D$ is the time dependent state variable acting as a boundary between the doped and undoped regions. As mentioned earlier, the memristor is initialized to R_{on} ($w = D$) such that it constitutes mostly of oxygen deficient TiO_{2-x}. Interaction of gases with the doped region changes R_{on} to R_{on_eff} without necessarily shifting the state variable.

The extent of change to the resistance of the doped region depends on the concentration and type of gas. The sensing capability of a single isolated memristor was verified with an oxidising gas. Fig. 2 shows a single memristor's response as a function of gas concentrations ranging from $0\,ppm$ to $10^4\,ppm$. Expectedly, the response rate increases with increasing gas concentration.

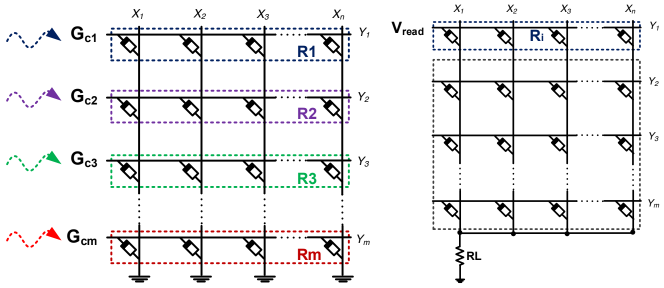
III. Gas Sensing with Crossbar Array

As earlier mentioned, the use of a single memristor cell as a sensor has been demonstrated experimentally in previous publications [9], [10] but single device sensors are usually susceptible to measurement errors due to issues such as a) instability of sensor response, b) irreproducibility of the sensor response among different devices and c) difficulty in maintaining high resolution response over a range of gas concentration. Causes of measurement errors in sensors could be reduced statistically by taking multiple measurements from the same sensor or from different independent sensors [5]. Array of sensors also open up the possibility of detecting multiple gases in real time. The use of MOSFET based sensors in an array to improve performance was demonstrated in [11], where pairs of Pd- and Pt-gate MOSFET were used to detect and analysis gas mixtures. Similarly, the use of commercially available SnO_2 sensors in an array to detect and differentiate organic compounds was also explored in [12]. These array of sensors make it possible to detect, quantify and differentiate multiple gases in real time. Memristor-based memory are often designed with crossbar architecture because of the possibility of building highly dense memory. The crossbar architecture consists of set of parallel nanowires perpendicularly placed on another set of parallel nanowires with a memristor cell inserted at every intersecting point of the wires. Each set of parallel wires represents the bit-lines and word-lines. In order to sense the resistance of a memristor in a crossbar memory array, a read voltage V_{read} (less than the threshold voltage to switch the memristor) is applied to either the word-line or bit-line and the other line is grounded through a load resistor. The other lines can be left floating. However, this simple sensing technique could introduce sneak-path problem that hinders independent sensing of each device in the array [13] In the next section, we propose a sneak-path free sensing mechanism for measuring the device's resistance.

A. Multi-Gas with m ($1 \times n$) Sensor Array

This section proposes a crossbar structure suitable for sensing multiple gases. A matrix of memristor sensors are designed such that memristors in same row have identical initial properties that enables them to react in approximately similar pattern in the presence of any target gas. In this architecture, each row in the matrix acts as a sensor. The number of gases that can be sensed using this architecture depends on the number of rows in the crossbar as shown in Fig. 3a. The number of sensing devices in each row can be determined based on the level of redundancies or samples needed in order to decide the properties of the target gas.

All the memristors in a row will have approximately similar resistance value because of their identical initial conditions with possible variations and we assume negligible line resistance. The sneak-path effect can be eliminated in this structure by sensing all memristors in each of the rows simultaneously as shown in Fig. 3b. Also note that when the resistance value of each row is being sensed, all other memristors in the array are shunted out of the circuit and they do not contribute to



(a) (b)

Fig. 3. (a) An $m \times n$ array of multiple sensors able to detect m different gases. (b) Reading technique for the multi-sensing structure.

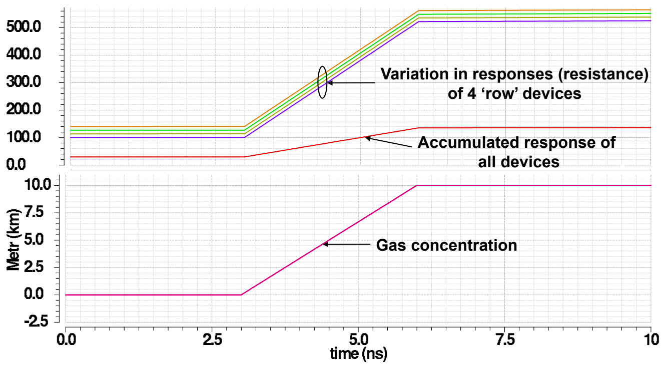


Fig. 4. Simulation result of exposing a row from a 4×4 memristor crossbar array to a range of gas concentration.

the sensed output. m number of reads is required to detect the response of all the sensors in the $m \times n$ crossbar.

Fig. 4 shows the experimental result from directing a range of reducing gas concentration to a row of a 4×4 sensor array. The initial resistance value of the 4 memristors in the target row was set to $100\Omega, 123\Omega, 127\Omega$ and 140Ω, representing an extreme case of almost 33% variation between the smallest and largest memristance. Despite the large variation, an average response (red waveform) which represents the parallel combination of the for memristor was measured by the sensing architecture over the range of gas concentration (pink waveform). If all the rows in the crossbar are used for gas sensing, measurements will be done by a succession of m read steps for $i = 1, ..., m$ and all responses recorded accordingly. The sensing structure depicted by Fig. 3 also makes it possible to design a fault tolerant system by introducing a repair mechanism that addresses faulty sensors in the array. This can be achieved by checking if the response of a memristor (sensor) considerably differs from the rest, in such case, the resistance of the cell can be set to a high resistance state or such cell substituted with a spare one.

IV. Discussion and Conclusion

To the best of our knowledge, this is the first attempt to develop a framework for multiple gas sensing with memristor crossbar. The $m(1 \times n)$ structure introduced prove to be efficient in terms of responsivity and reliability but at the expense of more devices. We believe that the proposed analysis represents a fundamental cornerstone to the success of this novel approach to sensing: future developments include the manufacturing, analysis, and modeling of prototypes based on the proposed architectures. Other alternative structures under consideration includes $m \times n$ (a single sensor made of mn devices) and the use of isolating devices in the $m \times n$ structures in order to achieve mn independent sensors. The effect of resistance variations in memristors in the row will also introduce a different dynamics that will requires further analysis. These sensing approaches are essential for integrating very dense sensor arrays on well known and established memory-like architectures already proposed for memristive arrays.

References

[1] Q. Wang, Y. Pan, S. Huang, S. Ren, P. Li, and J. Li, "Resistive and capacitive response of nitrogen-doped TiO_2 nanotubes film humidity sensor," *Nanotechnology*, vol. 22, no. 2, p. 025501, 2011.

[2] G. F. Fine *et al.*, "Metal oxide semi-conductor gas sensors in environmental monitoring," *Sensors*, vol. 10, no. 6, pp. 5469–5502, 2010.

[3] D. B. Strukov *et al.*, "The missing memristor found," *nature*, vol. 453, no. 7191, pp. 80–83, 2008.

[4] N. Barsan, C. Simion, T. Heine, S. Pokhrel, and U. Weimar, "Modeling of sensing and transduction for p-type semiconducting metal oxide based gas sensors," *Journal of Electroceramics*, vol. 25, no. 1, pp. 11–19, 2010.

[5] J. Fraden, *Handbook of modern sensors: physics, designs, and applications*. Springer Science & Business Media, 2004.

[6] J. Bai and B. Zhou, "Titanium dioxide nanomaterials for sensor applications," *Chemical reviews*, vol. 114, no. 19, pp. 10 131–10 176, 2014.

[7] S. Naisbitt *et al.*, "A microstructural model of semiconducting gas sensor response: The effects of sintering temperature on the response of chromium titanate (CTO) to carbon monoxide," *Sensors and Actuators B: Chemical*, vol. 114, no. 2, pp. 969–977, 2006.

[8] R. Binions *et al.*, "Zeolite-modified discriminating gas sensors," *Journal of The Electrochemical Society*, vol. 156, no. 3, pp. J46–J51, 2009.

[9] F. Puppo, A. Dave, M.-A. Doucey, D. Sacchetto, C. Baj-Rossi, Y. Leblebici, G. De Micheli, and S. Carrara, "Memristive biosensors under varying humidity conditions," *NanoBioscience, IEEE Transactions on*, vol. 13, no. 1, pp. 19–30, 2014.

[10] S. Carrara *et al.*, "Memristive-biosensors: A new detection method by using nanofabricated memristors," *Sensors and Actuators B: Chemical*, vol. 171, pp. 449–457, 2012.

[11] H. Sundgren, I. Lundström, F. Winquist, I. Lukkari, R. Carlsson, and S. Wold, "Evaluation of a multiple gas mixture with a simple mosfet gas sensor array and pattern recognition," *Sensors and Actuators B: Chemical*, vol. 2, no. 2, pp. 115–123, 1990.

[12] E. J. Wolfrum, R. M. Meglen, D. Peterson, and J. Sluiter, "Metal oxide sensor arrays for the detection, differentiation, and quantification of volatile organic compounds at sub-parts-per-million concentration levels," *Sensors and Actuators B: Chemical*, vol. 115, no. 1, pp. 322–329, 2006.

[13] E. Linn, R. Rosezin, C. Kügeler, and R. Waser, "Complementary resistive switches for passive nanocrossbar memories," *Nature materials*, vol. 9, no. 5, pp. 403–406, 2010.