Design and Fabrication of Memristors

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***Abstract*—This paper details the design and fabrication of memristors in the RIT Semiconductor and Microsystem Fabrication Laboratory. Two methods of partially oxidizing titanium were explored, reactive sputtering and thermal oxidation. It is determined that thermal oxidation allows for greater control over the oxidation process due to an inability to sufficiently control the gas flow in the sputter chamber. Electron beam lithography is used to define holes in oxide in which the memristors will be fabricated. Due to issues with the lithography, fabrication is incomplete and ongoing.**

I. INTRODUCTION/THEORY

THE existence of a fourth fundamental circuit element, complementary to the resistor, was theorized by Leon Chua in a 1971 paper [1] that examined the relationships between charge and flux in resistors, capacitors, and inductors. He predicted that the device would provide a relationship between magnetic flux and charge similar to the relationship a resistor provides between voltage and current, as shown in Fig. 1, adopted from Strukov [2]. The device would act as a resistor whose value varied relative to the current passing through it. Whatever value the device was at when current flow stopped would remain static; the resistor would "remember" whatever state it was left in, thus the "memristor".

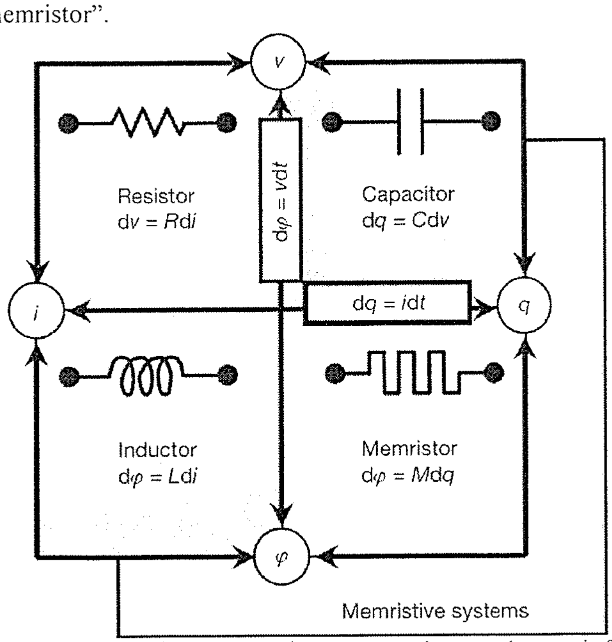


Fig. 1. The relationships between voltage, current, charge, and magnetic flux produced by the three established fundamental circuit elements and the proposed fourth element, the memristor [2].

Of particular interest is that the function of this device cannot be duplicated by any combination of the other three fundamental circuit elements [2]. In 2008, 37 years after the publication of Chua's paper, researchers at HP labs published a paper of their own reporting the fabrication of working memristors. Their devices utilized a partially oxidized titanium film on top of a completely oxidized titanium film, such that the oxygen deficiencies acted as positive charge carriers that could be redistributed throughout the entire stack by applying positive or negative voltage. Movement of these deficiencies, as shown in Fig. 2 (adopted from Williams [3]), affected the resistance of the stack.

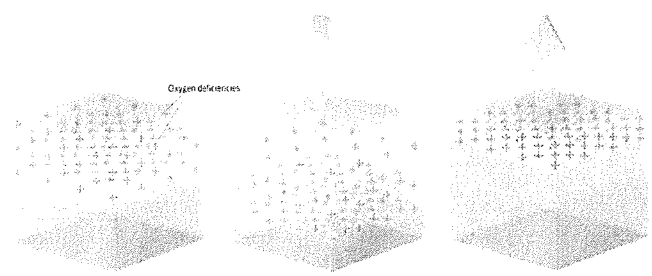


Fig. 2. Mechanism of memristor function [3]. Oxygen deficiencies in TiO_{2-x} are electron donors, acting as positive charge carriers. Their distribution within the stack is controlled with applied voltage.

This behavior produces a unique I-V characteristic. Fig. 3 shows the I-V curve predicted by Dr. Chua and Fig. 4 shows the actual I-V curve obtained by R.S. Williams at HP. Following the I-V curve in the positive direction, it can be seen that it acts like a typical resistor until it reaches some threshold, at which point the voltage is sufficiently positive to repel the positive charge carriers, distributing them throughout the stack. This provides a path for charge to flow, decreasing the overall resistance. This state is shown in the center cube of Fig. 2. Following the curve in the negative direction, we see that again, the memristor functions as a typical resistor until it reaches some negative threshold, at which point the voltage is sufficiently negative to attract the positive charge carriers, grouping them together as seen in the rightmost cube in Fig. 2. This decreases the charge paths through the stack, increasing its resistance.

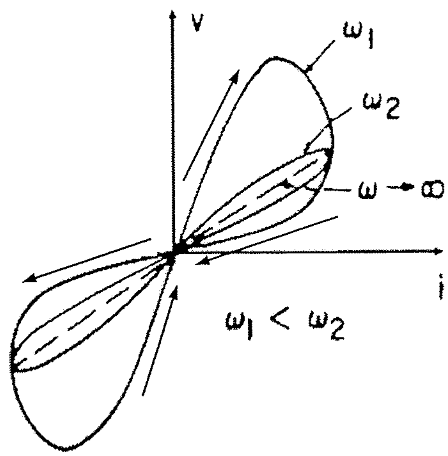


Fig. 3. Hypothetical memristor behavior predicted by Leon Chua [3], the man who first predicted the existence of the device. Arrows show the direction of voltage change.

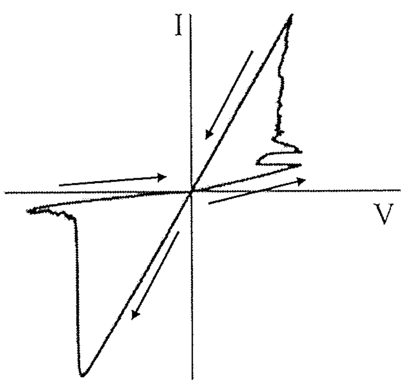


Fig. 4. Experimental results from R.S. Williams' testing of memristors [3]. It can be seen that as charge flows through the device, current flow increases until it reaches a maximum (minimum resistance). As voltage decreases and becomes negative, current decreases until it reaches a minimum (maximum resistance).

II. Processing/Results

The focus of this project has been to develop a process flow for fabricating memristive devices reminiscent of those created by the engineers at HP. The intended material stack is shown in Fig. 9. This undertaking has been challenging, requiring the development of processes that have never been attempted here at RIT, particularly the controlled partial oxidation of titanium. Two methods were explored to produce the desired thin film of oxygen deficient TiO_2 (TiO_{2-X}). The first was the use of reactive sputtering. Titanium was reactively sputtered onto silicon wafers with varying levels of argon and oxygen flow. The ratios of Ar:O_2 during the four depositions were as follows: 79:1, 78:2, 77:3, and 76:4. The electrical properties of the films were measured by the use of 4-point probing in conjunction with profilometry, yielding resistivity values (in Ω·μm) of 3.54, 19.79, 6.71, and "open", respectively [see Table I].

TABLE I
Reactive Sputtering Conditions and Results

Sample	Ar:O_2	Thickness (Å)	Rate (Å/s)	Resistivity (Ω-μm)
1	79:1	5,510	11.5	3.54
2	78:2	890	1.9	19.79
3	77:3	400	0.8	6.71
4	76:4	500	1.0	Open

Deposition conditions and associated results from process characterization of TiO_{2-X} reactive sputtering. All depositions were eight minutes in length with a constant chamber pressure of 8 mTorr.

The second method was thermal oxidation of a sputtered titanium film. The first wafer from the reactive sputtering samples, having a resistivity of 3.54 Ω·μm, was determined to be unoxidized titanium. It was cleaved in half, then one of the halves into fourths. The four samples were thermally oxidized in a rapid thermal processing (RTP) oven at 600, 700, 800, and 900 °C for ten minutes each with an oxygen gas flow of 10 sccm. Deposition conditions are summarized in Table II. A gradient in color between the samples was optically observed, higher temperature oxidations appearing hazier and lighter in color than cooler ones. This change in appearance represents varying degrees of oxidation. All samples were measured to have "open" resistivity values when characterized on the 4-point probe.

TABLE II
Thermal Oxidation Conditions

Sample	Temperature (°C)	O_2 Flow (sccm)	Time (minutes)
1	600	10	10
2	700	10	10
3	800	10	10
4	900	10	10

Deposition conditions for thermal oxidation testing. All samples were electrically "open" when sheet resistance was measured with the 4-point probe.

Memristance exhibits an inverse square relationship to size. In other words, memristance is one million times as important at the nanometer level than it is at the micrometer level. [3] It is therefore beneficial to fabricate the smallest possible devices. To do this, electron beam lithography was used to define circles in oxide, into which holes will be etched and the devices will be fabricated. The circles range in radii from 50 nm to 20 μm. A photograph of the entire pattern after the first develop attempt is shown in Fig. 6. Features as small as 50 nm in radium were visible. Unfortunately, the resist was not exposed with a high enough dose to allow proper development, preventing completion of this project at the present time. It can be seen in Figs. 7 and 8 that even after developing for ten times as long as usual, the resist still remains.

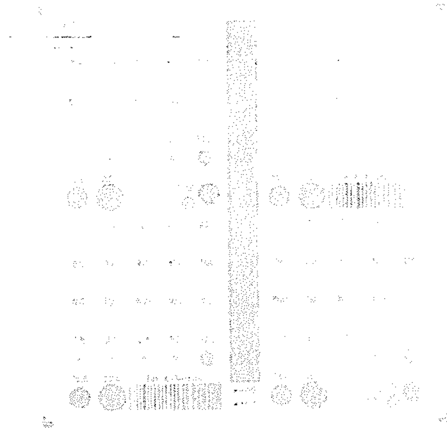
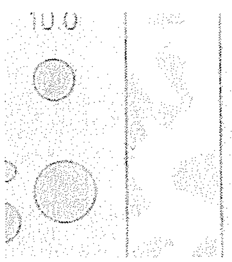


Fig. 6. Microscope image of the electron beam lithography pattern used. Labels refer to the radii of their corresponding circles. Radii range in size from 50 nm to 20 μm.



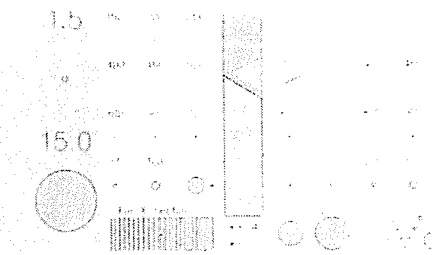


Fig. 7. (Left) It can be seen that even after excessive development, the resist is wrinkling on the larger features, but not developing. No change is visible on the smaller features, which are necessary for device fabrication.

Fig. 8. (Right) In some cases, the resist is peeling off, but still, even after excessive development, it is not dissolving as expected.

Once the lithography issue is resolved, the processing will be completed. The material stack that will be deposited is shown in Fig. 9. The device will be fabricated on a p-type wafer to ensure ohmic contact to the bottom metal electrode. The depositions are as follows. First, a bottom aluminum electrode is sputtered, 500 Å thick. This is followed by sputtering a 500 Å layer of pure titanium which will be thermally oxidized to produce TiO_{2-X}. Next, 500 Å of TiO_2 is sputtered, followed by a top aluminum electrode of 1000 Å, also sputtered. Finally, a backside aluminum contact of arbitrary thickness is sputtered. It is expected that this process will produce functioning memristors.

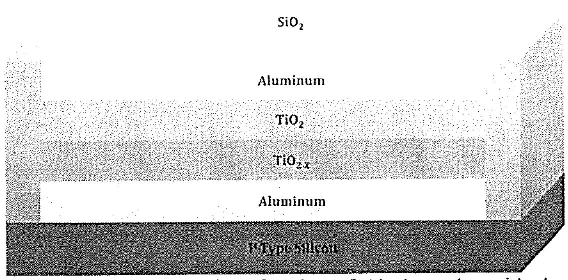


Fig. 9. Memristor project design. Consists of Al electrodes with thermally partially oxidized sputtered Ti and reactively sputtered TiO_2 device layers. Stack is deposited into an e-beam defined hole in SiO_2.

III. Conclusion

Two methods of partial oxidation of titanium have been explored and it has been determined that thermal oxidation is a more controllable process for RIT's cleanroom facility. It is possible, however, that increasing the gas flows and controlling the total pressure with the sputter chamber throttle valve could help to make reactive sputtering a more controllable method. This should be investigated, as it would prevent the need for a high temperature thermal oxidation step which could create problems with the bottom aluminum electrode.

In addition to characterizing processes to partially oxidize titanium films, a process flow for memristor fabrication that can be carried out in nearly any semiconductor fabrication facility has been developed.

Acknowledgments

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References

[1] L.O. Chua. "Memristor – The Missing Circuit Element," *IEEE Transactions on Circuit Theory*, vol. CT-18, no. 5, pp. 507-519, September 1971

[2] D.B. Strukov, G.S. Snider, D.R. Stewart, and R.S. Williams, "The missing memristor found," *Nature*, vol. 453, pp. 80-83, May 2008

[3] R.S. Williams. "How We Found the Missing Memristor," *IEEE Spectrum*, vol. 45, no. 12, pp. 28-35, December 2008