A Flexible Solution-Processed Memristor

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***Abstract*—A rewriteable low-power operation nonvolatile physically flexible memristor device is demonstrated. The active component of the device is inexpensively fabricated at room temperature by spinning a TiO_2 sol gel on a commercially available polymer sheet. The device exhibits memory behavior consistent with a memristor, demonstrates an on/off ratio greater than 10 000 : 1, is nonvolatile for over 1.2×10^6 s, requires less than 10 V, and is still operational after being physically flexed more than 4000 times.**

***Index Terms*—Flexible electronics, flexible memory, memristor, sol gel, titanium dioxide.**

I. Introduction

WE HAVE fabricated a physically flexible solution-processed device that exhibits electrical behavior consistent with that of a memristor, a memory device recently experimentally demonstrated and proposed to be the missing fourth basic circuit element [1], [2]. Although electrical switching behavior has been observed from organic monolayers and metal oxides from as early 1968 [3]–[11], the unique electrical characteristics associated with the memristor have the potential to revolutionize computing. For example, the functionality of a memristor has been compared to that of a neurological synapse; thus, memristors may eventually enable electronic computation functionally similar that which occurs in the human brain [12]. We have fabricated devices that demonstrate these desirable memristor characteristics as well as: physical flexibility, fabrication by using inexpensive room-temperature solution processing, operation voltages of less than 10 V (relatively low power for flexible electronics), on/off ratios greater than 10 000 : 1, memory potential that is nonvolatile for over 1.2×10^6 s, and the ability to be operated after being physically flexed 4000 times. These characteristics make our flexible memristor device a prime candidate for use in inexpensive flexible lightweight portable electronics, such as disposable sensors [13]–[17].

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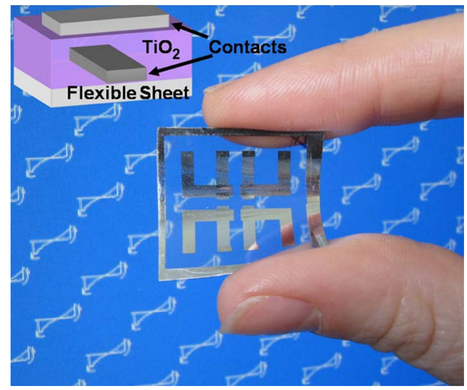

Fig. 1. Flexible polymer sheet patterned with four rewriteable nonvolatile flexible TiO_2 sol gel memory devices with cross-bar aluminum contacts. The inset is a side view cartoon of the flexible TiO_2 device structure.

II. Experiment

Rather than using expensive methods and equipment for the deposition of the active TiO_2 layer of our device, we performed a room-temperature deposition through a spin-on sol gel process that required no annealing [18]. This procedure consists of spinning a titanium isopropoxide solution on the flexible plastic substrate (spun on at a rate of approximately 33 r/s for 60 s), and then leaving the precursor in air for at least 1 h to hydrolyze and form a 60-nm-thick amorphous TiO_2 film [18]. To electrically contact the active area, a simple two-terminal crossbar is formed by depositing the bottom contact (80 nm Al) on the substrate (approximately 2.5 cm $\times$ 2.5 cm square of HP color laserjet transparency C2934A) prior to spinning the precursor, and depositing the top contact (80 nm Al) after the precursor has hydrolyzed. The devices presented in this letter were fabricated by depositing the top and bottom metal contacts via thermal evaporation through a shadow mask; however, there is the potential to deposit contacts from solution to enable roll-to-roll or inkjet processing [19]. The final $Al/TiO_2/Al$ stack has an area of approximately 2 mm $\times$ 2 mm and is shown in Fig. 1.

III. Results and Discussion

The flexible TiO_2-based devices exhibit electrical switching with memory characteristics that match the electrical behavior reported for memristors [1], [2]. A representative example of the basic switching behavior is shown in Fig. 2. On the first voltage sweep (1), the device starts in the low-conductivity state until the bias is increased to approximately +3 V, when the

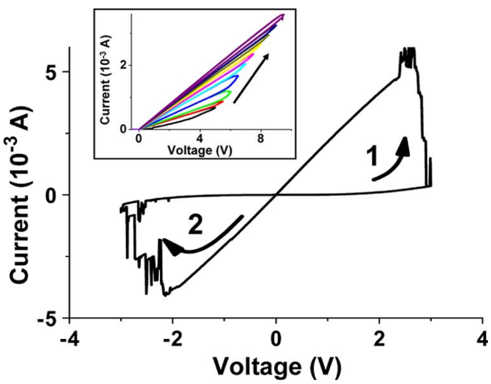

Fig. 2. Current versus voltage for one switching cycle of a device. The inset shows sweeps of the same bias polarity applied consecutively (i.e., consecutive "writes" with no "erasing") to a previously unbiased device, demonstrating a decrease in device resistance with each sweep as the device transitions from a low to high state in multiple steps. The electrical results shown in the inset are from a different device than those shown in the body of the figure. For measurements, the current compliance was 50 mA, and the voltage compliance was 10 V.

current abruptly transitions to a high conductivity state ("write"). This state remains until a negative bias of approximately -2 V is applied (2), resulting in a transition back to a low-conductivity state ("erase"). The initial "write" of a device can be achieved by applying either an adequate positive or adequate negative bias through a voltage sweep or pulse; however, once this initial switch is performed, the opposite polarity is required to "erase." These devices also showed relatively high yields. Of the 50 devices that were fabricated over seven different experimental runs, 42 devices exhibited electrical behavior indicative of electrical switching (overall yield of 84%) with the 16% of devices that did not show switching behavior as electrical "shorts" $(R < 50\ \Omega)$. The 50 switching devices exhibited a median "write" bias magnitude of $|2.8| \pm 1.3$ V, a median "erase" bias magnitude of $|4.0| \pm 1.4$ V, a median high state resistance of $1.1 \times 10^3\ \Omega$, and a median low state resistance of $2.7 \times 10^7\ \Omega$. We performed multiple switching cycles on devices and observed switching between high and low states with resistance values similar to those of the original cycles.

These electrical results are consistent with the theorized memristor mechanism, the drift of oxygen vacancies in the TiO_2 under bias [1]–[3], [20]. Although it is possible that this vacancy drift occurs through a single filament rather than a frontlike system, filament switching generally results in binary electrical characteristics [4]. While our devices can be operated as binary switches ("hard switching"), they can also be operated in the "soft switching" regime where consecutive bias sweeps of the same polarity result in a step-down in resistance with each sweep. For example, the inset of Fig. 2 demonstrates "soft switching" with voltage sweeps of the same polarity consecutively applied to a previously unbiased device (i.e., multiple "writes" applied in a row without "erasing" in-between). As these consecutive sweeps are applied, the device transitions from a low to high state in multiple steps, which is consistent with the simulated theoretical electrical behavior of a memristor in the "soft switching" regime [1]. The complete details of the switching mechanism of the memristor are explored in great detail elsewhere [1], [2], [21].

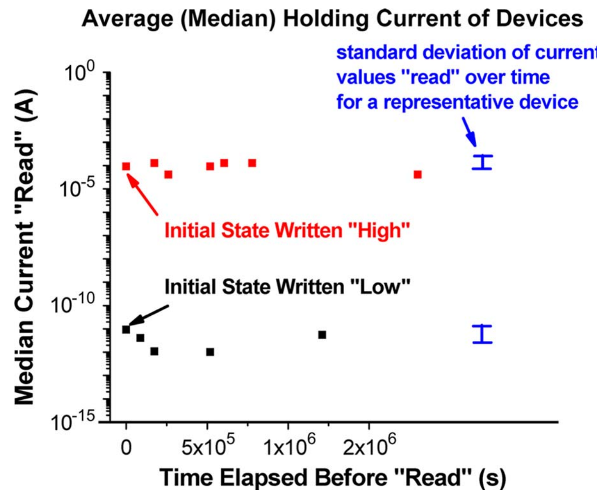

Fig. 3. Median current at 0.25 V from several devices initially set in the "high" state and "read" (by applying 0.25 V) at various time increments, and the median current from several devices initially set in the "low" state and then "read" at various time increments. Moreover, shown on the graph is the standard deviation of the current values "read" at all elapsed times for a representative device initially set in the "high" state and for a representative device initially set in the "low" state.

Although our TiO_2 film was deposited by using a nontraditional sol gel method, the unbiased film was determined via X-ray photoelectron spectroscopy to have the same chemical composition as that of reported memristors [22]. Additionally, although there has been some question as to the origin of switching in devices with aluminum contacts [23], the switching behavior from our devices cannot be attributed to the aluminum (or aluminum oxide), since it was also observed from devices with noble metal (gold, silver, and platinum) contacts. Furthermore, the devices still exhibited switching behavior when placed under vacuum overnight and then electrically characterized in an argon environment, which indicates that the behavior is not ambient dependent. The switching was also observed when a glass substrate was used instead of a polymer sheet, indicating that while using the polymer sheet demonstrates the potential of the devices to be used as flexible substrates, the switching mechanism is not intrinsic to it.

The memory of the devices remained nonvolatile for more than 1.2×10^6 s (14 days). To characterize the volatility of the flexible memristors, several devices were first each set "high" or "low" by applying voltage sweeps of the appropriate polarity until the device resistance was consistent with previously observed values for the respective state. These states were then "read" (by applying 0.25 V) on day 0, and periodically over time. Fig. 3 shows the median current "read" over time from the devices initially set "high," as well as the median "read" over time from the devices initially set in "low." The error bars to the right of the graph indicate the standard deviation of the current over the same time scale for a representative device initially set in the "high" state and for a representative device initially set in the "low" state. As these data show, the average device demonstrates no noticeable change in the current magnitude of the set state even after more than 1.2×10^6 s (14 days).

To demonstrate mechanical robustness, the devices were electrically characterized after being physically flexed with an automated flexing apparatus. The flexing apparatus gripped

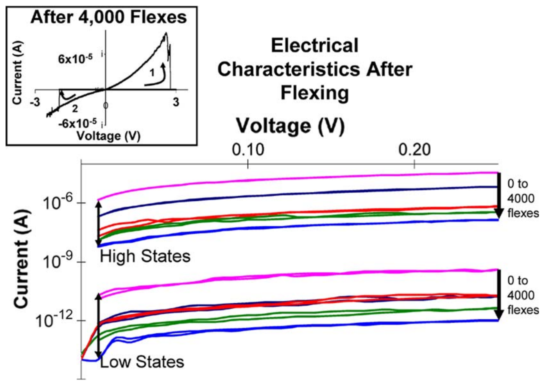

Fig. 4. Representative "read" current versus voltage for the devices after being set into a high current state. The current states were "read" after 0 flexes, 100 flexes, 2000 flexes, 3000 flexes, and 4000 flexes (total), and repeated after the devices were set low. The ratio of the high state current to low state current, for high and low states flexed an equal number of cycles after being set, remains at least 10 000 : 1. The inset shows a cycle of switching for a device that has been flexed more than 4000 times, demonstrating that the devices are still operational after switching.

the edges of the sample and flexed the device from flat to a half-ellipse with a semiminor axis of 2.5 mm and a semimajor axis of 8.5 mm. For the flexing measurements, several devices were "written," flexed 100 times, and then the current state was read by applying a voltage of 0.25 V. The current state was then read again after 1900 more flexes (2000 total), and then again after every 1000 flexes until the devices were each flexed for a total of 4000 times. At this point, an adequate negative bias was applied to each device to switch it into the low state (erased), and the flex/read cycles described above were repeated. Fig. 4 shows representative read current versus voltage for the devices after flexing. As evident in this graph, both the high and low states decreased by about half of an order of magnitude with each 1000 flexes. Yet, the ratio of the high state current to low state current, for high and low states flexed an equal number of cycles after being set, remains at least 10 000 : 1. This demonstrates that even after flexing 4000 times the devices retain an adequate state ratio for memory applications. The inset of Fig. 4 is a cycle of switching for a device that has been flexed more than 4000 times, demonstrating that the devices are still operational after significant flexing.

IV. Conclusion

We have described the fabrication and electrical behavior of a simple inexpensive solution-processed low-power device for flexible nonvolatile memory. Prototypical devices demonstrate on : off ratios greater than 10 000 : 1 that hold for over 1.2×10^6 s (14 days) and after 4000 flexes. For simplicity, the device's contacts were evaporated, but there is the potential for depositing the contacts from a liquid source (such as printing) for completely roll-to-roll processing. These memristor devices have the potential for use as flexible memory components, enabling a paradigm shift in electronics toward inexpensive lightweight portable physically flexible technologies.

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