INVITED PAPER

Memristors With Flexible Electronic Applications

This paper discusses how to fabricate memristors on flexible polymer substrates for applications in lightweight, inexpensive, and flexible electronics products.

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ABSTRACT | In addition to the potential for memristors to be used in logic, memory, smart interconnects, and biologically inspired architectures that could transform traditional silicon-based computing, memristors may enable such transformative technologies on physically flexible substrates. The simple structure of a memristor, which generally consists of a thin film of oxide sandwiched between two metal contacts, contributes to its compatibility with existing and future large area flexible electronics. This is especially true considering that recent work has demonstrated the ability for titanium dioxide-based memristors to be deposited from solution at room temperature by using a sol gel technique on a flexible polymer substrate. The integration of memristors with traditional flexible devices (such as thin-film organic, zinc oxide, or amorphous-Si transistors) may enable the realization of a new paradigm in computing technology through lightweight, inexpensive, flexible electronics.

KEYWORDS | Flexible electronics; flexible memory; memristor; resistive memory

I. INTRODUCTION

The field of flexible electronics has the potential to revolutionize portable inexpensive electronics, but requires the development of both memory and computational logic components that can be integrated on flexible substrates in a reliable manner. While organic field-effect transistors (FETs) have shown promise for use in computational logic [1]–[3], the majority of flexible memory devices that have been reported, such as write-once-read-many-times (WORM) polymer devices [4]–[6] and three terminal polymer-based ferroelectric memory devices [7]–[10], do not address the needs of a rewritable, low-power flexible memory device. This void in the field of flexible electronics has been highlighted by the International Electronics Manufacturing Initiative (iNEMI) technology roadmap [3]. One possibility for filling this void is through the development of flexible memristors, which have been identified as promising devices by the International Technology Roadmap for Semiconductors (ITRS) [11].

The memristor is a novel electronic component [12]–[24] that was first experimentally identified based on the electrical switching observed from an inflexible, TiO_2-based, two-terminal device [14]–[16]. Although similar electrical behavior has been observed since 1968 from metal–oxide films [25]–[31] and crossbar memory devices containing organic molecules and Ti/TiO_x [32]–[35], the link between the experimental switching and theoretical memristive behavior was only made relatively recently [14]–[16]. Since then, the electrical behavior of the memristor has gained attention due to its unique potential applications including: biologically inspired computing [16], [20], logical computation [17], [21], and/or applications in smart interconnects [19]. The realization of flexible memristors could enable not only a route for the unique applications of memristors in flexible versions (e.g., flexible smart interconnects), but because memristors also possess qualities required for basic binary memory, flexible memristors also have the potential to meet a need in the flexible electronics community as basic nonvolatile memory.

While the concept of "flexible memristors" is novel and few devices have been directly identified as such [18], [36],

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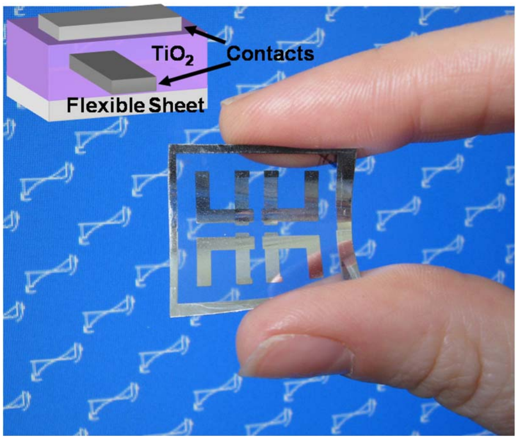

Fig. 1. ***Top view of four flexible memristors and a side view of the flexible memristor structure. Reprinted with permission from [18].***

there are technologies that might have the potential to be adapted for flexible memristor applications. One example of a physically flexible memristor is shown in Fig. 1. The electrical behavior of flexible memristive technologies has been shown to be similar to their inflexible counterparts [18], [36]. Therefore, if the technologies and processes used to fabricate inflexible memristive devices could be modified to be compatible with flexible substrates, there may be the potential for the transfer of memristive technology to a flexible substrate. For example, TiO_2, which has been deemed responsible for the memristive behavior in many devices [14]–[16], can be processed at room temperature through the use of a sol gel [18], [36]. This room temperature processing enables the deposition of TiO_2 on flexible polymer substrates that would be degraded by processing at higher temperatures. It is thus worthwhile to explore inflexible technologies that may have the potential to be adapted to function on flexible substrates. This paper explores memristor technologies, evaluating their potential to contribute to the future development of flexible memristors for basic flexible memory and for more revolutionary flexible memristor applications.

We discuss technologies for their potential to be used as a flexible memristor with both traditional memory and novel logic applications. In order for a device to be a memristor with the potential for both unique memory and logic applications, it must A) be a two-terminal device, B) be switched between two distinctive resistance states through the application of two different bias magnitudes or polarities, C) hold each respective resistance state once the bias is removed (be nonvolatile), D) still be nonvolatile with the application of a relatively small bias (as compared to the switching bias) of either polarity, and E) switch at a bias less than 10 V. In reviewing existing devices with the potential for flexible applications in terms of these constraints, we observed that they generally fall into one of three categories: 1) devices that exhibit bipolar nonvolatile switching, 2) devices that exhibit unipolar nonvolatile switching, and 3) organic devices that may have potential for use in flexible technologies, but that exhibit other switching.

II. DEVICES THAT EXHIBIT BIPOLAR NONVOLATILE SWITCHING

The first experimentally observed behavior directly linked to theoretical memristance was reported from a two-terminal crossbar structure with a TiO_2 layer less than 1 μm thick sandwiched between two metal contacts on an inflexible substrate [14]. This memristive behavior consists of bias-dependent switching between two different resistance states. The switching is dependent on the polarity of the bias (i.e., an opposite bias is required to switch the device "OFF" as is required to switch the device "ON") and is thus known as "bipolar" switching. Since the device holds the respective resistance state once switched, even if the bias is no longer applied, it is also nonvolatile. Other groups have observed similar bipolar nonvolatile switching from two-terminal crossbar structures with thin-film metal oxides [37]–[40] or other variations of oxide-based structures [41]–[43] but did not identify the behavior as consistent with the theoretical memristor. Current–voltage curves that are representative of bipolar switching are shown in Fig. 2. The I–V curves in Fig. 2 are clearly bipolar

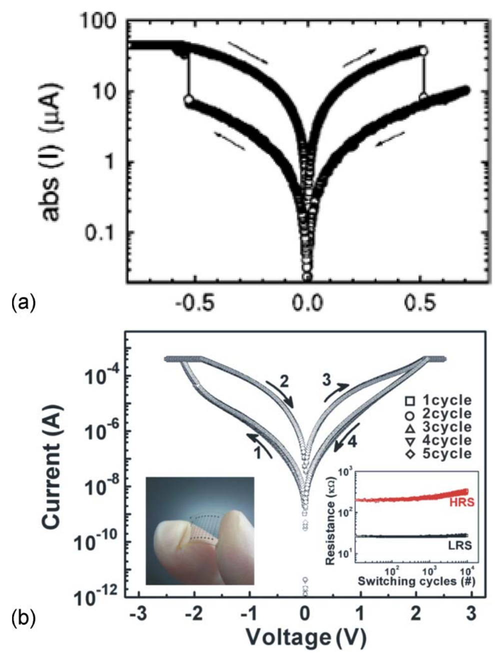

Fig. 2. ***Bipolar switching consistent with memristor behavior is evident for (a) an inflexible SrZrO device. Reprinted with permission from [27] © 2000, American Institute of Physics. (b) Similar bipolar switching is also evident for flexible Al/TiO_2/Al devices formed on polyethersulfone. Reprinted with permission from [46] © 2010, IOP Publishing, Ltd.***

in that the devices switched from a relatively low current to a higher current state upon the application of an adequate negative bias, and then they held this high current state until the application of an adequate positive bias. The behavior from these devices is consistent with what would be required for memory since they are nonvolatile and can be switched between two resistance states through the application of two different bias polarities. Additionally, these devices exhibit characteristics that could be useful in novel logic applications, such as in logical computation based on material implication [21]. These electrical characteristics include that they are: two terminal, can be switched between two different states upon the application of opposite polarity biases of magnitudes less than 10 V, and they hold these respective states even when the bias is removed or an adequately small bias (less than the switching bias) of either polarity is applied [21].

There has been recent work fabricating nonvolatile, bipolar, switching devices on flexible substrates [18], [36], [44]–[57]. The fabrication of these flexible devices has been enabled by the simple structure of memristors. By forming these thin films and metal contacts through processes that are compatible with flexible substrates and technologies the interesting binary characteristics can be translated to flexible technologies. Examples of compatible formation processes are deposition through sol gel [18], [36], spin casting using a dispersed solution [51], [52], [55], atomic layer deposition [44], [46], [53], or sputter deposition [14]–[16], [57]. The electrical characteristics of these flexible devices can be comparable to their inflexible counterparts [Fig. 2(b)].

While the specifics behind the switching mechanism are not completely understood and may vary depending on the device structure, the nonvolatile bipolar switching observed from metal oxide devices has been generally attributed to anion migration [14]–[16], [18], [30], [35]–[37], [40], [41], [43], [44], [49], [52], [53], [55], [57]. The basic theory behind the anion migration mechanism is that, upon the application of adequate bias or charge, a conductive ion path forms between the two contacts to create a lower resistance "ON" state. This ion path can then be broken through the application of an adequate opposite bias or charge flow to return the device to the original higher resistance "OFF" state [14]–[16], [18], [30], [35]–[37], [40], [41], [43], [44], [49], [52], [53], [55], [57]. Anion migration has been suggested to be the origin of bipolar switching in devices fabricated on either flexible [18], [36], [44], [52], [53], [55], [57] or standard substrates [14]–[16], [30], [35], [37], [40], [41], [43], [49]. Thus, the switching mechanism seems to be independent of the flexibility of the substrate on which the device was fabricated.

There is evidence that some of the same devices that exhibit bipolar switching also exhibit unipolar switching under different measurement conditions [38], [40], [43]–[45], [56], [58]. It is suggested that these devices exhibiting both unipolar and bipolar switching are dominated by a different mechanism for each type of switching. For example, when the unipolar switching is observed, it has been reported that the electrical behavior is dominated by a filament mechanism [38], [40], [45], [58] as discussed in Section III.

Overall, bipolar nonvolatile devices represent an extremely promising sector of potentially flexible memristors. Their electrical characteristics are consistent with the first reports of memristor behavior [14]–[16] and have been already observed in physically flexible devices [18], [36], [44]–[57]. The problems that plague these devices are similar to problems of the memristor community in general; mostly, a lack of reliability, variability between devices, and the looming question of a detailed switching mechanism. Since these problems are not unique to the flexible electronics community, broader efforts to solve them for memristors in general have the potential to advance flexible technologies as well. Additionally, because many of these inflexible devices are oxide-based [14]–[16], [23], [24], [37]–[40] and there are several oxides that can be formed through flex-friendly processes including atomic layer deposition, sputter deposition, and sol gel methods, there is the potential to expand the types of thin films used in an effort to explore improving device performance.

III. DEVICES THAT EXHIBIT UNIPOLAR NONVOLATILE SWITCHING

A unipolar resistive switching device is a device that can be switched between two resistance states by using the same polarity [59]. Although memristive behavior in devices is typically identified by a bipolar nonvolatile switching event in the *I–V* curve [13], [60] (also known as a "pinched-hysteresis loop" [13], [60] or a "bow tie curve" [16]), unipolar switching devices may still satisfy the criteria defined in Section I for unique memory and logic applications. Several studies have recently appeared in which unipolar switching devices were fabricated on flexible substrates [31], [44], [45], [58], [61]–[65]. An example of a flexible unipolar switching device is shown in Fig. 3. Several other unipolar switching devices fabricated on standard substrates could also be relevant to flexible electronics technology [28], [29], [38], [40], [66]–[70].

Typical unipolar resistive switching characteristics from a flexible device are shown in Fig. 3(b), and switching characteristics from an inflexible unipolar switching device are shown in Fig. 4. In each case, the device begins in a high-resistance state (HRS) and the bias is increased until the *I–V* spontaneously jumps to a higher current (at $\approx$2.5 V and $\approx$1.5 V for Figs. 3 and 4, respectively). At this point, the device is in the low-resistance state (LRS), as is evident upon the second bias ramp (which begins at 0 V). Eventually, upon increasing the bias again, the device switches back to the HRS (at $\approx$1.0 V and 0.6 V for Figs. 3 and 4, respectively). By comparing Fig. 3 to Fig. 4, it is evident that flexible unipolar switching devices may have

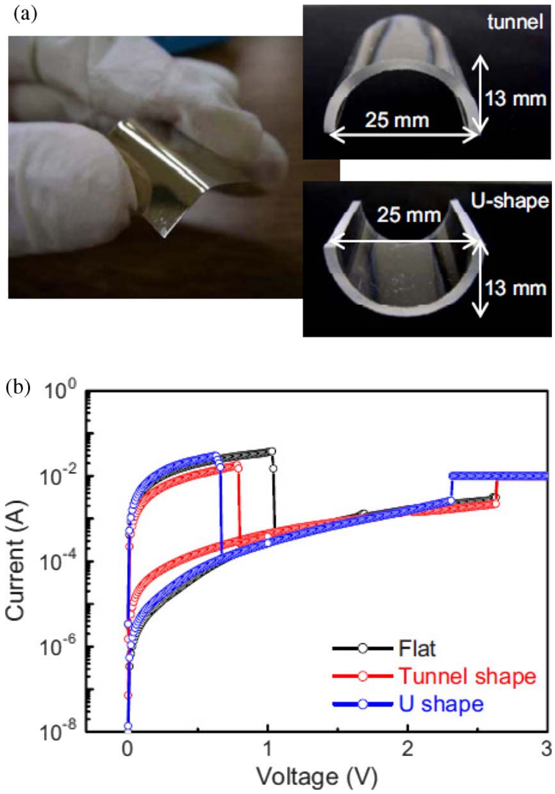

Fig. 3. ***(a) Photograph of a flexible ZnO unipolar resistive switching device being flexed. (b) Typical switching characteristics for the device shown in (a). Reprinted with permission from [45] © 2009, American Institute of Physics.***

the same general switching characteristics as inflexible devices. Furthermore, the device shown in Fig. 3 uses ZnO as the switching media, while the device in Fig. 4 uses NiO, which suggests that there is no significant difference between the general unipolar switching characteristics of devices fabricated with different oxides.

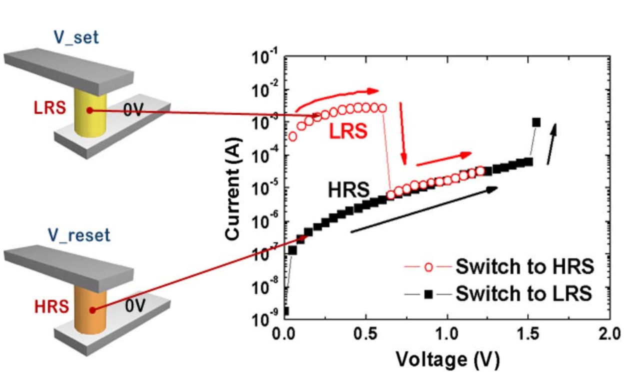

Fig. 4. ***Schematic diagram and typical switching characteristics of an inflexible NiO unipolar resistive switching device. Ramps for switching to the LRS and back to the HRS are shown. Reprinted with permission from [29] © 2008, Wiley-VCH Verlag GmbH & Co.***

Therefore, it is not surprising that unipolar switching devices have been fabricated from several different oxides, and that the same oxides have been used to fabricate both flexible and inflexible devices. TiO_2 [28], [38], [44], [62], [68] and Al_2O_3 [31], [67] have been used for both flexible and inflexible devices. ZnO [45], [63], [64] and NiO [29], [40] have also been used for flexible and inflexible devices, while HfO_2 [28] and SiO_2 [28], [69], [70] have been used in inflexible devices. It is important to also note that oxides are not always the switching medium in these devices; for example, granular metal layers surrounded by semiconducting polymers have also been used in inflexible devices [66]. Ultimately, the choice of switching material is important as it may affect the device operation parameters (V_{SET}, V_{RESET}, and R_{LOW}/R_{HIGH}).

The switching mechanism most often cited as the origin of unipolar nonvolatile switching is the formation and rupture of either single [31], [39], [40], [58], [62] or multiple [29], [38], [43]–[45], [63], [67], [68] filaments of conductive material. Electroforming is usually, but not always, performed in order to initiate formation of these filaments [31], [40], [43], [44], [62], [64], [68], [69]. The formation of these filaments leads to an increased electrical conduction between contacts, causing the device to switch from the HRS ("OFF") to the LRS ("ON"). These filaments are usually described as being composed of either metallic atoms [39], [58], [68] or charged vacancies [31], [44], [62], [63]. The devices switch back to the OFF state as a result of either Joule heating [29], [31], [45] or a chemical reaction [29], [70] leading to the rupture of the filament(s).

Additional switching mechanisms that have been proposed to explain unipolar resistive switching include: the generation and annihilation of potential barriers [27], electrochemical migration at the interface [71], charge trapping [65], [66], [72], and a "random circuit breaker network" model [73]. Additionally, not all studies explicitly identify a switching mechanism [64]. For devices that exhibit both unipolar and bipolar resistive switching, a different mechanism has been attributed to each mode [38], [40], [45], [58].

It is particularly important for devices that will be used in flexible electronics that the switching characteristics be unaffected by the flexing of the devices [31], [44], [58], [62], [64], [65]. As shown in Fig. 3, the device still exhibits unipolar resistive switching even while being bent. As shown in Fig. 5, switching between the high resistance and low resistance in a similar device is preserved regardless of the radius of bending or the number of times the substrate is flexed.

Despite the fact that unipolar devices are often not identified as memristors, the devices in this section all meet the five criteria in Section I for potential memristive applications in logic and memory. Each of the devices has two terminals (criterion A) that can be switched from an HRS to an LRS (criterion B) with a relatively low bias (criterion E). Each device is nonvolatile (criterion C), even

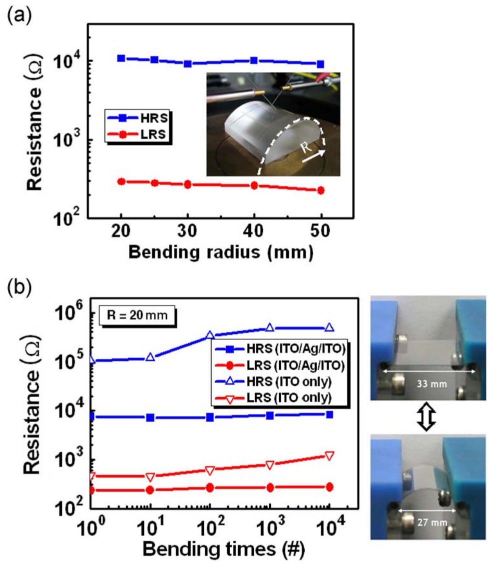

Fig. 5. ***(a) HRS and LRS data from a flexible ZnO unipolar resistive switching device as a function of the bending radius. (b) Data for the HRS and LRS following multiple flexes at*** $R = 20$ ***mm. Reprinted with permission from [64] © 2009, American Institute of Physics.***

when relatively small biases are applied (criteria D). While not all the studies projected an ultimate retention time, some show no significant degradation or change in R_{LOW}/R_{HIGH} ratios through retentions of 10^2 [29], [38], [40], [70], 10^4 [31], [44], [62], [65], 10^5 [63], [64], [69], and 10^6 s [58]. Furthermore, based on their results, Kim *et al.* [63], Seo *et al.* [64], and Yao *et al.* [69] extrapolated retention times for their devices of ten years. The R_{LOW}/R_{HIGH} ratios have been shown to be stable through 10^2 [29], [63], [64], [68] and 10^4 switching cycles [31], [58], [69], regardless of whether the substrates are flexible. Examples of data retention and endurance tests are shown in Fig. 6.

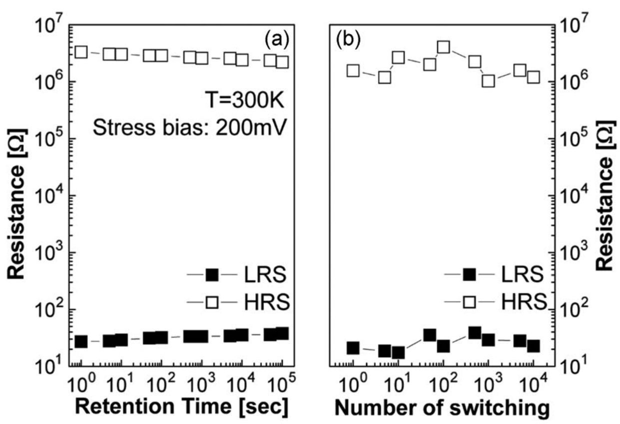

Fig. 6. ***(a) Data retention characteristics for a flexible ZnO unipolar resistive switching device over time. (b) Endurance tests. Reprinted with permission from [63].***

The electrical characteristics of unipolar switching devices demonstrate their potential for use in promising memristor applications, such as in computational logic [17], [21] and artificial synapses [16], [20]. The primary disadvantage to using unipolar resistive devices in such circuits is that there is a significantly wide distribution of operating voltages, decreasing reliability [73]. However, this disadvantage is also observed from bipolar and other resistive switching devices. Additionally, it may be possible to reduce the range of operating voltages by controllably creating defects in the switching medium [73] or adding intermediate layers that would help stabilize filament formation and rupture [74].

IV. ORGANIC SWITCHING DEVICES

In reviewing potential technologies that may contribute to the development of a flexible memristor, it is essential to include organic switching devices. Organic devices are important to flexible technology due to the inherent flexibility of their polymer components [61], [75], the versatility of their chemical structure [4], [75], their generally low cost and light weight [4], [61], [75], [76], as well as the prospects for simplified manufacturing [61]. As such, organic materials have been integrated into some large scale mass production processes [5], [61], [75], [76], and organic switching/memory devices could be integrated into flexible technology [10].

One category of organic switching/memory device is a device based on blends of semiconductor and ferroelectric polymers [10], [77], [78]. These ferroelectric blend devices [10], [77], [78] typically exhibit memory effects driven by their inherent ferroelectric polarization, making it impossible to change its conductivity independent of its polarization [10], [78]. In this respect, ferroelectric devices differ from the memristive systems discussed in Sections II and III. Asadi *et al.* fabricated ferroelectric polymer networks sandwiched between metal electrodes for use in nonvolatile memory [10], [77], [78]. The switching mechanism in these devices is different from the mechanisms discussed in Sections II and III. Switching in these ferroelectric devices relies on controlling the height of the injection barrier between the contacts and the polymer using the polarization charge [77].

While the switching mechanism for ferroelectric devices is completely different from that of oxide-based devices, their electrical characteristics appear to be similar. Ferroelectric devices have two terminals (criterion A) and they exhibit retention times in excess of 11 days (criterion C). Although the ferroelectric polymer devices switch between two different rectifying states when two different polarities of biases are applied [10], [77] (criterion B), their switching characteristics only exhibit significant hysteresis under the application of relatively large biases. These required high-switching biases could be

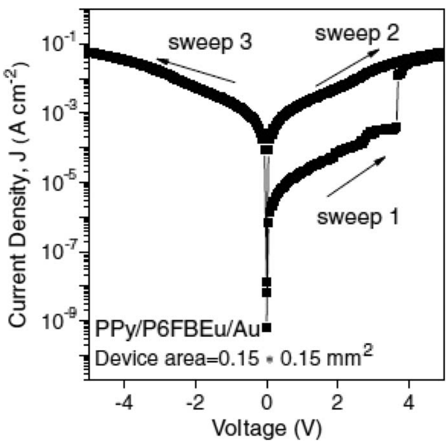

Fig. 7. ***Switching characteristics of a flexible polymer WORM device. Reprinted with permission from [5] © 2007, Elsevier.***

problematic for applications in unique memristive devices, such as logic [21] or neuromorphic systems [20].

Another device that has been demonstrated to have the potential to be fabricated on flexible substrates and to demonstrate switching is the organic WORM device [4], [5], [61], [75], [76], [79], [80]. In these devices, their behavior is controlled by the chemical structure of the polymer film. Organic WORM devices can be switched from an HRS to an LRS only once, as shown in Fig. 7. In these devices, switching from the HRS to the LRS is attributed to an electric field-induced lowering of the energy barrier to electron injection [4], [5], [61]. Organic WORM devices are effective nonvolatile memory because once such a device is switched into the LRS it will remain in that state, potentially for over one year [5]. However, because WORM devices can only be switched once, instead of back and forth between HRS and LRS (criterion B), there would be difficulty in using WORM devices in the unique memristive memory and logic applications under consideration.

V. CONCLUSION

While few flexible memory technologies have been officially declared "memristors," there are numerous bipolar and unipolar resistive switching devices that meet the criteria necessary for memristor logic and memory applications and that either are fabricated on flexible substrates or may have the potential for transfer to flexible substrates. The main limiting factor in realizing these technologies appears to be no different than the main limiting factor in the realization of "traditional" memristor devices on inflexible substrates: reproductibility and reliability. These issues may stem from processing variations in device fabrication, or they may be a symptom of the need for an improved understanding of the devices' switching mechanisms. Once device reproducibility and reliability are improved, which may be pushed along through work with inflexible memristors, flexible memristors have the potential to revolutionize electronics, not only through the unique characteristics of the memristor, but also through the application of these unique characteristics to flexible technologies. ■

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