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The Memristive Properties of a Single VO_2 Nanowire with Switching Controlled by Self-Heating

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The development of low-power and high-density memory devices has attracted considerable interest with integrated circuit technology because of the physical limits of scalability in traditional memory devices, such as dynamic random access memory (DRAM). Rationally designed materials and technologies have been the subjects of active research for the next generation of universal memories. A memory device should exhibit not only a high capacity and low power consumption but also high-speed operation and long retention based on simple structures.[1] Recently, a memristor capable of behaving as the two-terminal non-volatile and switchable resistive memory was demonstrated, which is well known as the fourth fundamental circuit element theoretically predicted by L. Chua in 1791.[2] Since memristors can achieve both high integration density and low switching power consumption thanks to high scalability down to only a few nanometers, they have been one of the most attractive devices for next-generation memory technology.[3] Various materials with switchable and retainable resistance have been used to realize the memristor memory, including proteins,[4,5] TiO_2,[6] polyaniline,[7] Si,[8] MgO,[9,10] and VO_2.[11–14] VO_2 is one of the most notable materials owing to its fast response time and large range of accessible resistance values through a metal-to-insulator transition (MIT). MIT, which is based on the structural phase transition between metallic tetragonal rutile (VO_2(R)) and insulating monoclinic structure (VO_2(M)), can lead to change in electrical resistance of about four orders of magnitude and pinched hysteresis loops in the current–voltage (*I*–*V*) curve.[15–19] The temperature at which this MIT occurs can be changed by doping, lattice mismatch, external strain, and controlling grain size.[20–26] Over the years, memristors based on thin-film VO_2 have been demonstrated as the memory device with switchable and retainable resistances. The change of resistance was obtained by providing pulse-type energy sources, such as voltage, light, and current,[12–14] that played the part of a trigger for MIT. The resistance could be retained by keeping the temperature near the transition temperature (T_c) of about 68 °C using an additional heating source. However, although the switched resistance can be maintained well near the T_c, it can provide only a small range of accessible resistance of less than two orders of magnitude at fixed temperature because only a part of the hysteresis is used.[12–14] Furthermore, using additional heating source for maintaining the resistance can make it difficult to achieve low power consumption and high-density integration. Thus, it is necessary to develop innovative strategy towards achieving a low-power, high-density, and two-terminal memristor for practical application in non-volatile memory device.

For the first time, we report a two-terminal memristor memory based on a single VO_2 nanowire that can not only provide switchable resistances in a large range of about four orders of magnitude but can also maintain the resistances by a low bias voltage. The VO_2 nanowires were synthesized by hydrothermal method, followed by thermal annealing process to form monoclinic VO_2 phase. X-ray diffraction (XRD) and differential scanning calorimetry (DSC) results showed that the nanowires consisted of a monoclinic VO_2 phase without any hydrate phases and that the MIT occurred at 68 °C in a heating cycle, respectively. The phase transition of the single VO_2 nanowire was driven by the bias voltage of 0.34 V without using any heating source. The memristive behavior of the single VO_2 nanowire was confirmed by observing the switching and non-volatile properties of resistances when voltage pulses and low bias voltage were applied, respectively. Furthermore, multiple retainable resistances in a large range of about four orders of magnitude can be utilized by controlling the number and the amount of voltage pulses under the low bias voltage. This is a key step towards the development of new low-power and two-terminal memory devices for next-generation non-volatile memories.

For low-power, high-density, and non-volatile memristor memory, it is important to make a two-terminal device without using any additional heating source. Thus, we focused our research on designing a single VO_2 nanowire-based memristor with a pinched hysteresis loop through self-Joule-heating generated by a low bias voltage. For the memristor based on a single VO_2 nanowire, VO_2(M) nanowires were synthesized by hydrothermal process.[27] **Figure 1**a shows field emission scanning electron microscopy (FESEM) images of nanowires, which were

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DOI: 10.1002/adma.201302511

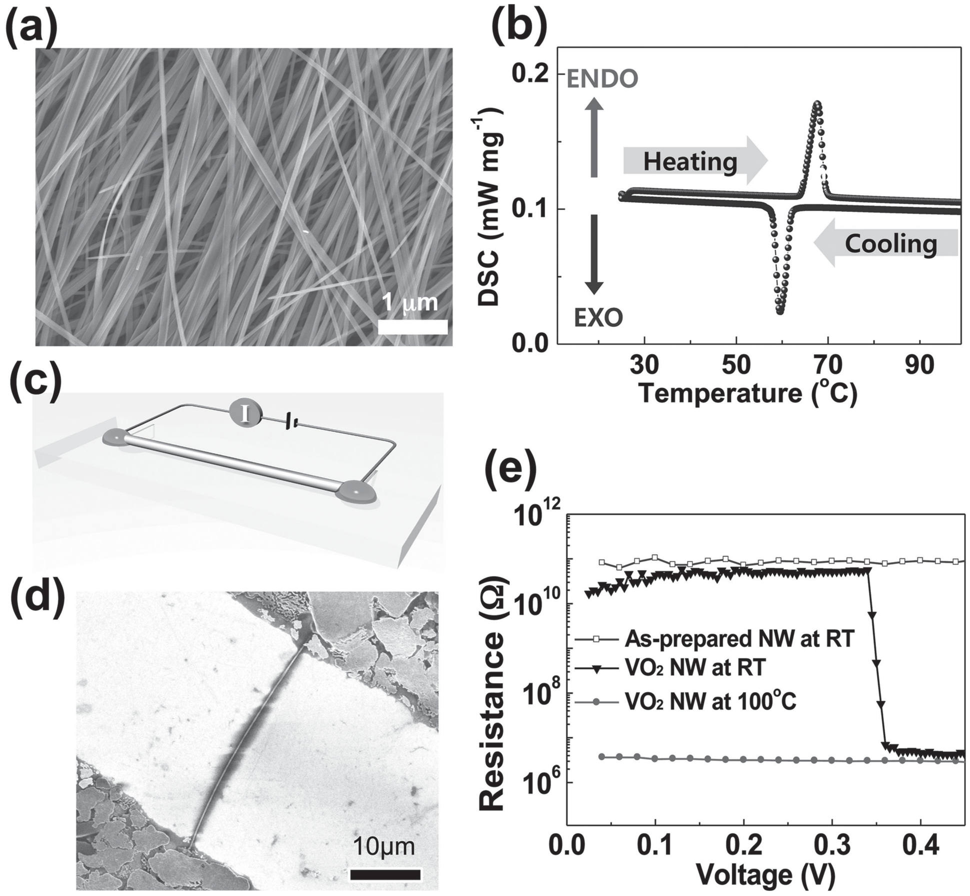

Figure 1. a) FESEM image of nanowires obtained by hydrothermal process followed by annealing for 4 hours at 400 °C in an N_2 atmosphere. b) Differential scanning colorimetry (DSC) results of annealed VO_2 nanowires. c) A schematic of the memristor device, which consists of a single VO_2 nanowire, voltage source, and ampere meter. d) A FESEM image of a single VO_2 nanowire and silver contact. e) Resistance with bias voltage of annealed VO_2 nanowires at room temperature (triangle), at 100 °C (circle), and an as-synthesized nanowire at room temperature (square).

synthesized by hydrothermal process for 3 days at 220 °C, followed by annealing for 4 hours at 400 °C in an N_2 atmosphere. After 3 days of the hydrothermal process, all of the VO_2 powder was changed into the nanowires with 80 to 160 nm diameters. And the XRD and thermogravimetric analysis (TGA) results showed no signs of the presence of second phases (including hydrate phases) in the annealed VO_2(M) nanowires (Figure S1, Supporting Information). To investigate MIT properties of annealed VO_2 nanowires, the DSC analysis was carried out, and the results are shown in Figure 1b. During the heating and cooling cycles, the endothermic and the exothermic peaks that come from the transitions of M $\rightarrow$ R and R $\rightarrow$ M are observed at ≈68 and ≈59 °C, respectively, which is similar to the reported values of VO_2.[15,17,28,29] This hysteretic behavior clearly shows that the VO_2 nanowires can exhibit the characteristic of the phase transition which is similar to that observed in VO_2 bulk. Figure 1c shows the schematic of the single VO_2 nanowire-based memristor of which the two ends were electrically connected to copper wires with silver paste. Two kinds of voltage sources were supplied: one is the bias voltage for measuring resistance, and the other is the voltage pulse for triggering MIT in the VO_2 nanowire. A single nanowire with length and thickness of ≈30 μm and ≈160 nm, respectively, was connected to the silver electrodes, as shown in Figure 1d.

To investigate the potential of the device for a heat-source-free memristor based on a single VO_2 nanowire, *I–V* curves of the single VO_2 nanowire were measured at room temperature and 100 °C, and the results are shown in Figure 1e. While the resistance of the as-synthesized nanowire without the annealing process was not changed with the bias voltage at room temperature, that of the annealed VO_2 nanowire was reduced by ≈4 orders of magnitude on M to R transition. It is probably due to the presence of hydrate phases in the as-synthesized nanowires that cannot drive the MIT. However, since the annealed nanowire is VO_2(M) without any hydrate phases, the MIT can be driven by the bias voltage, which can generate self-Joule heating. The resistance value of the annealed nanowire after the MIT with the bias voltage over ≈0.34 V at room temperature was similar to that obtained at 100 °C. This means that the MIT of the single VO_2 nanowire can be driven by the bias voltage as well as by direct heating. Furthermore, since the MIT of the single VO_2 nanowire took place with the low bias voltage of about 0.34 V in the resistance–voltage (R–V) curve owing to its extremely small volume, which is much lower than

DOI: 10.1002/adma.201302511

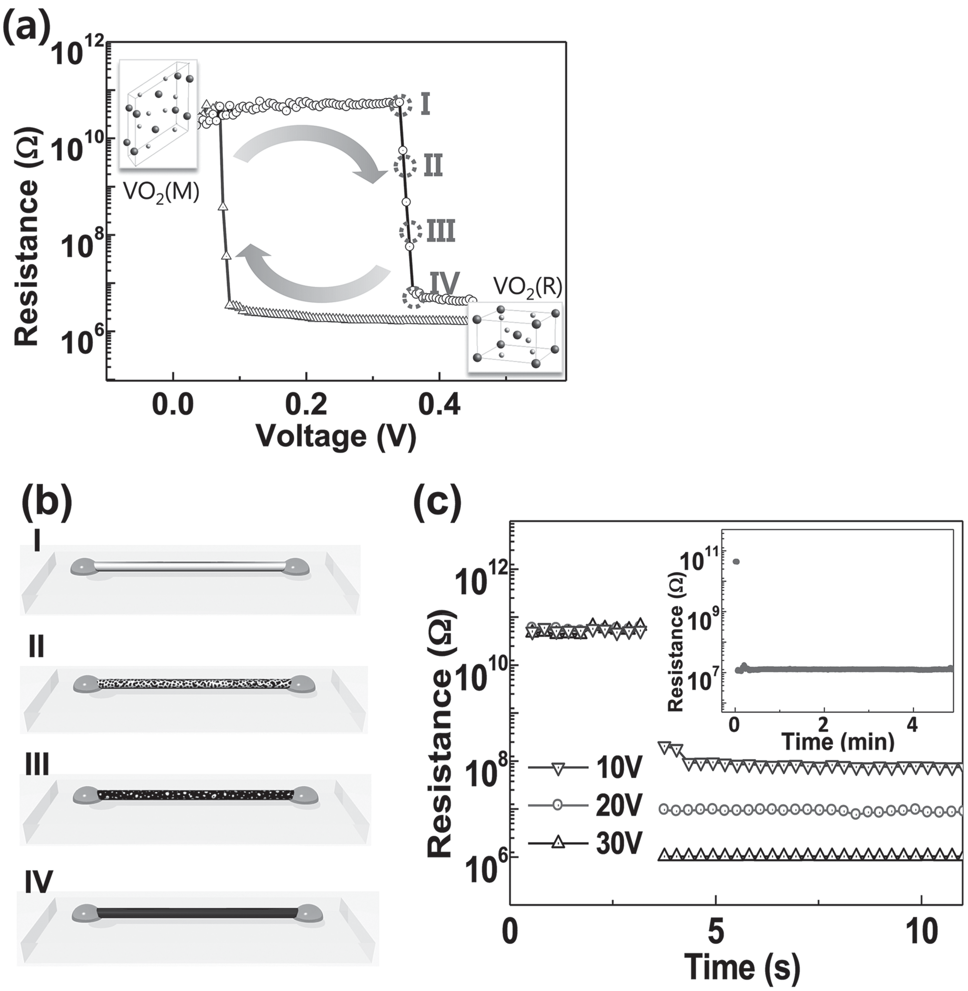

Figure 2. a) The resistance–voltage (*R–V*) hysteresis curve. Insets show the crystal structures of VO_2(M) and VO_2(R). b) Schematics showing the gradual change of phases inside the nanowire at different points marked in the *R–V* curve. Black and white parts denote the metallic and insulating phase of nanowire, respectively, and the mixed state shows the presence of multiple resistance of VO_2 nanowire. c) Resistance of annealed VO_2 nanowires at room temperature with 0.3 V voltage bias. The 30 V (diamond), 20 V (triangle), and 10 V voltage pulses (circle) are applied for 0.25 seconds. Inset graph shows the change of resistance for 5 minutes with 0.3 V voltage bias and 20 V voltage pulse.

those previously reported,[30–32] devices based on a single VO_2 nanowire can have the advantage of low power consumption.

For the memristor application of the single VO_2 nanowire, switchable and retainable resistance is needed. First, to confirm the potential of the retainable resistance, the hysteresis curve of the single nanowire was obtained by measuring the change of resistance with the bias voltage. As shown in **Figure 2**a, the MIT was induced by the Joule heating, and the hysteresis behavior was observed (the transition voltage for the M to R transition was larger than that for the R to M transition). This hysteresis behavior leads to the non-linear *I–V* characteristic and eventually enables the switched resistance to be maintained. It was reported that the switchable resistance can be obtained by realizing the mixed state of metallic and insulating phases in the VO_2.[12–14] If energy, such as heat or light, is large enough to drive MIT is applied to VO_2, all of the insulating phase (I in Figure 2b) can be transformed into metallic phase (IV). But when the applied energy is not large enough for the complete phase transition, the metallic phase can be partially formed in the insulating phase (II and III) owing to the percolative nature of the MIT in VO_2.[14,33,34] In other words, the mixed states of metallic and insulating phase can be obtained during the MIT of a single VO_2 nanowire, and the relative amount of each phase (metallic/insulating phase ratio) of the mixed state can be controlled by the amount of applied energy, which can lead to various resistance values.

Before demonstrating the retainable and switchable characteristic of a single VO_2 nanowire, it is necessary to determine the amount of bias voltage that can maintain the switched resistance through self-Joule heating. In previous results, the specific temperature, which can maintain the switched resistance, was determined between the two transition temperatures in heating and cooling cycle of the hysteresis in the R–T curve because the resistance can be changed only in the hysteresis loop.[12–14] Likewise, since the temperature of the nanowire can be controlled by self-Joule heating through the application of specific bias voltage,[35] to find out the amount of the specific bias voltage, we investigated the resistance change of the nanowire when different amounts of bias voltages were applied inside the hysteresis loop. When the bias voltage was over 0.3 V, the MIT took place over time because the temperature of the nanowire was increased over M to R transition temperature by Joule heating. When the bias voltage was below 0.3 V, the mixed state returned to the initial state (that is, the insulating state) over time because the nanowire was cooled below the R to M transition temperature. However, when the bias voltage of 0.3 V was applied in the nanowire, the M to R transition (I to II, III, and IV in Figure 2b) did not occur by the self-Joule heating (Figure S2, Supporting Information), and the resistance of the mixed state did not return to that of the initial state through R to M transition (II, III, IV to I). Using this specific bias voltage of 0.3 V, the retainable and switchable characteristics were realized by applying various voltage pulses for 0.25 seconds under the bias voltage. As shown in Figure 2c, the resistance rapidly dropped to lower values depending on the amount of the voltage pulse, and they were then maintained for over 5 minutes. In other words, when the 0.3 V bias voltage is applied at room temperature, the nanowire can be in the thermally stable state, in which the amount of the heat absorption in the nanowire by the self-Joule heating would be almost the same as that of heat desorption into the surrounding atmosphere. In the thermally stable state, the nanowire does not undergo M to R transition from the insulating state or R to M transition from the mixed state. Of course, the amount of the specific bias voltage, which can retain the switched resistance, may change depending on the dimension of nanowires and the ambient temperature, but this result clearly shows that the retainable and switchable characteristics in a single VO_2 nanowire can be realized by the application of voltages without using any additional heating source.

For practical device application, well-defined controllability of resistance based on the retainable and switchable characteristics is one of the most important requirements. For switching device application of VO_2, the MIT induced by external strain has been reported.[25,26] Under the same applied voltage, the low resistance status of the VO_2 single domain can be switched to a high resistance status by stretching the substrate. The VO_2 device of these previous works shows only two resistance states; however, the resistance of memristor can be changed into various values by a voltage pulse. The change of resistance was measured with the value of voltage pulses (1, 3, 5, and 10 V) and the number of voltage pulses (up to 10 times) of a single VO_2 nanowire, as shown in **Figure 3**. Before applying the voltage pulses, the VO_2 nanowire was in the insulating state

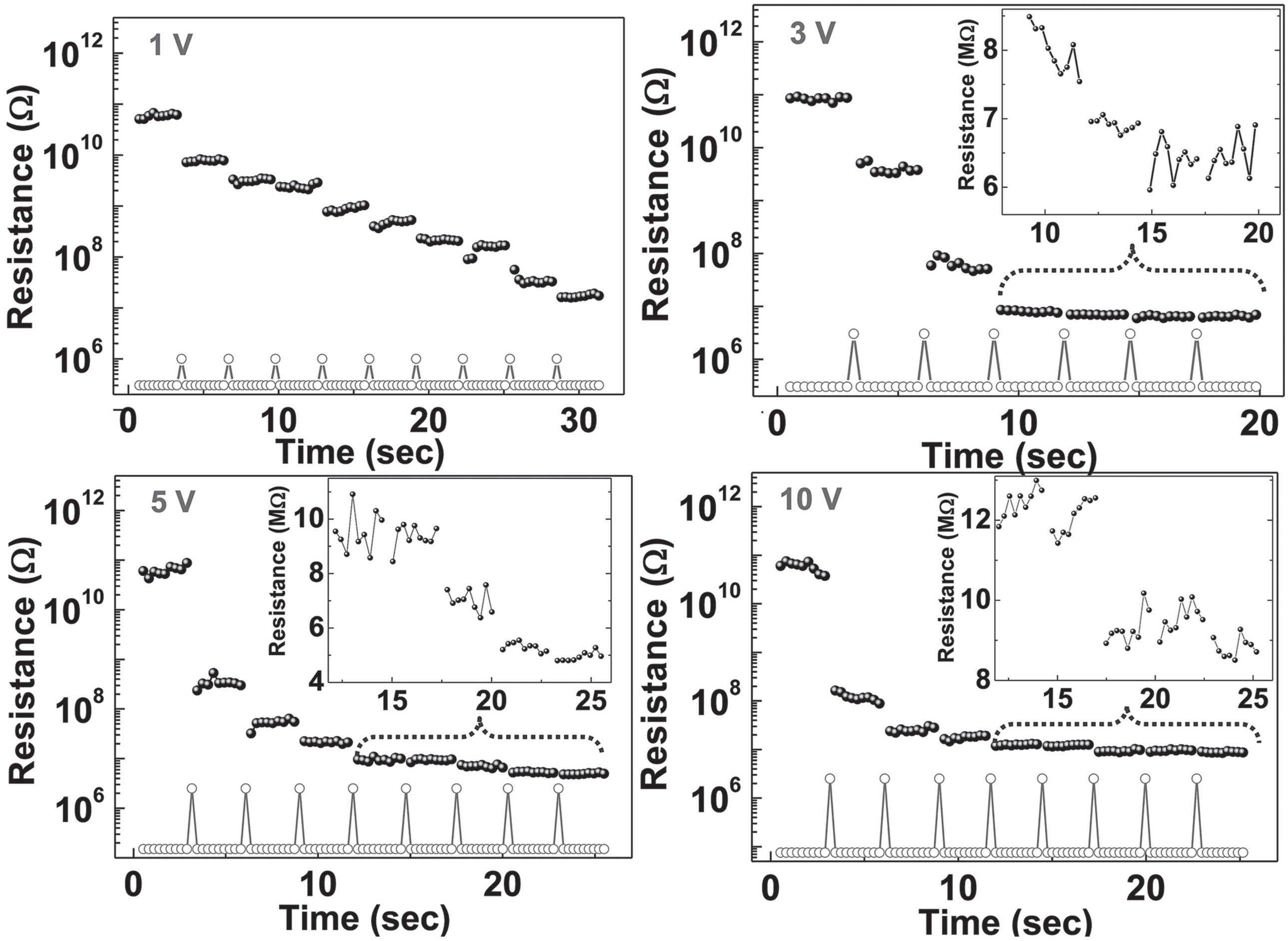

Figure 3. The change of resistance measured with the amount (1, 3, 5, and 10 V) and the number (up to 10 times) of voltage pulses of a single VO_2 nanowire. The well-defined multiple resistance values s with large range can be obtained by controlling the amount and the number of voltage pulse.

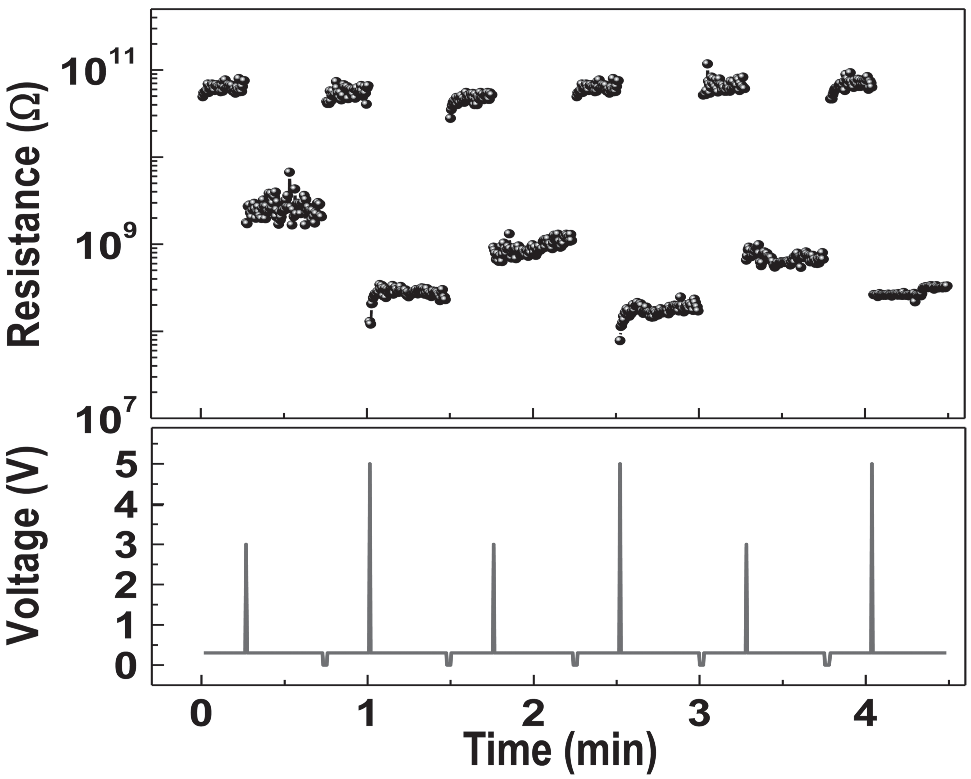

Figure 4. Demonstration of the information storage that shows reliable and non-volatile switching property of VO_2 single nanowire. The 0.3 V voltage bias is applied for reading, and the 3 and 5 V voltage pulses are applied for writing. The zero voltage is used for erasing and resetting to initial resistance.

which has a resistance of ≈10^{11} Ω. When the voltage pulse was applied to the single nanowire, the resistance dropped to lower value owing to the partial formation of the metallic phase in the insulating phase. This resistance drop can be obtained by low voltage pulse of 1 V, and as the amount of voltage pulse increases to 3, 5, and 10 V, the resistance can be decreased to values that are much lower than that of insulating state. Also, the resistance decreases in a step-by-step mode corresponding to the application of repeated voltage pulses. The change of resistance is largest when the first voltage pulse is applied and decreases as more pulses are applied, and the resistance is saturated to the value of ≈10^{7} Ω, which is the same as that of the metallic phase (IV in Figure 2b). As shown in the insets of Figure 3, the resistance shows switching property with changes of less than one order of magnitude near ≈10^{7} Ω. These results suggest that the amount of change in resistance can be controlled even within less than one order of magnitude by the amount and the number of voltage pulses. The total range of accessible resistance is approximately four orders of magnitude, which is similar to the change of resistance in MIT (that between I and IV in Figure 2b) of a single nanowire. In previous reports, the resistance was controlled by heating stage, and the ranges of accessible resistance at fixed temperature was less than two orders of magnitude because they could use only a part of the hysteresis loop.[12–14] However, when self-Joule heating is used instead of the direct heating with additional heat source, the nanowire can have a range of temperature, and any resistance value in between those of metallic and insulating states can be accessed.

The single VO_2 nanowire can be utilized in an information storage device owing to its switchable and retainable resistance that can be easily controlled by applying voltage. To investigate the applicability of the single VO_2 nanowire in the information storage device, we measured the change of resistance that is the result of the voltage pulse for writing and the zero voltage for erasing and resetting. The changes of the resistance of a single VO_2 nanowire when two different voltage pulses are applied repeatedly are shown in **Figure 4**. The initial state (at room temperature without voltage pulse) of the VO_2 single nanowire is insulating state (~10^{11} Ω), and two different values of resistance are obtained by applying voltage pulse of 3 and 5 V for 0.25 second under the bias voltage of 0.3 V. The 3 and 5 V voltage pulses decrease the resistance by over 1 and 2 orders of magnitude, respectively. And the resistances can be retained for over 25 seconds by bias voltage. Considering the resistance change with less than one order of magnitude in the previous report,[12–14] this large change of resistance can help to obtain reliable switching performance in the information storage application. As has already been explained in Figure 3, the change of resistance is largest when the first voltage pulse is applied, and as it approaches the metallic state, more energy is required to achieve new lower resistance states. Therefore, the reliable switching property with large resistance change by low voltage pulse can be successfully achieved by setting the state of VO_2 nanowire near the insulating state. The voltage pulse under bias voltage, however, can drive only one-way transformation (M to R transition). To reset VO_2 into the initial state, different operations, such as zero bias voltage, are needed. Applying zero voltage bias to the VO_2 nanowire for two seconds can reset nanowire to the initial state. After resetting, the resistances can be switched reproducibly by applying voltage pulse under the bias voltage. This shows that the VO_2 nanowire, when the change of resistance is controlled by the self-Joule heating, has the advantage of having access to wide range of resistances and obtaining reliable resistance switches, which can lead to a high-performance non-volatile memory switch device with improved stability and operating speed.

In summary, to demonstrate a two-terminal memristor for next-generation non-volatile memory, the non-volatile switchable resistance of a single VO_2 nanowire, which was synthesized by hydrothermal process and thermal annealing, was investigated. The retainable and switchable resistance characteristics with a wide range of accessible resistance can be successfully controlled with low voltage. This characteristic is connected with the percolative nature of the MIT; the mixed state of metallic and insulating phases in VO_2 material. The low voltage bias can maintain the resistances in the entire temperature range in which MIT occurs owing to self-Joule heating. Self-Joule heating can bring accessible resistance within a range of four orders and reliable switching characteristic over one order of magnitude of resistance change. By applying zero-bias voltage, the resistance can be reset to the initial insulating state. The resistivity changes for writing with voltage pulse and erasing with zero-bias voltage show very high reproducibility. This is the first report of the memristor based on a single VO_2 nanowire. And it is also the first report of a simple two-terminal memristor that can be operated by voltage source without using any additional heating source or voltage pulse, bias voltage, zero bias voltage for writing, reading, and erasing, respectively, with retainable resistance. The development of a switch memory device based on VO_2 nanowire that can be operated by voltage source can open perspectives for low power consumption, low-cost fabrication process, high density, and high performance with reliable and non-volatile switching characteristics in the memristor applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Research supported by grant from Construction Technology Innovation Program (CTIP) funded by Ministry of Land, Transport and Maritime Affairs (MLTM) of the Korean Government, (grant no. 12CCTI-B050622–05–000000) and by the LG Yonam Culture Foundation, MANA, the World Premier International Research Center Initiative (WPI Initiative), MEXT, Japan, through a satellite laboratory at Georgia Tech.

Received: June 13, 2013
Published online:

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DOI: 10.1002/adma.201302511