

# Resistance Switching Capable Polymer Nanocomposites Employing Networks of One-Dimensional Nanocarbon Wrapped by TiO<sub>2</sub> Conformal Layer

Woojin Jeon , Youngjin Kim, and Sang-Soo Lee 

**Abstract**—In order to impart resistance switching capability to polymer-based composite, one-dimensional conductive nanomaterials such as carbon nanotube (CNT) and carbon nanofiber (CNF) were wrapped with TiO<sub>2</sub> conformal layer for passivation, and embedded in polymer matrix to form a networklike distribution within it. The CNT-TiO<sub>2</sub> and CNF-TiO<sub>2</sub>-embedded composites, respectively, exhibited the reproducible resistance switching behavior of the high on/off ratio, along with the good switching stability under repetitive switching measurements. Furthermore, it is notable that the presence of defect site or incomplete formation of the TiO<sub>2</sub> passivation layer on the conductive component would significantly alter the switching performance. The advantages of our approach include the simple and mass-production capable fabrication procedure along with the sustainable switching performance suitable to promising nonvolatile memory device applications.

**Index Terms**—Carbon nanotubes and nanofibers, electrical properties, nanocomposites, resistance switching.

## I. INTRODUCTION

AS AN alternative for dynamic random access memory (DRAM) or flash memory, several types of new memory devices including ferroelectric RAM (FeRAM), magnetoresistive RAM (MRAM), phase-change RAM (PCRAM), and resistance switching RAM (RRAM) have been suggested [1]–[3]. Among them, RRAM based on resistance switching phenomena in metal-insulator-metal (MIM) structures, has been intensively

researched in recent years as a promising next generation memory candidate due to the nature of high operation speed, low power consumption, non-volatility, simple structure, and similarity to conventional Si-based process [4]–[12].

To date the studies to impart flexibility to RRAM devices have been reported by several research groups [13]–[19]. One of the methods for producing flexible RRAM is the deposition of transition metal oxide, as thin as can be bent, onto flexible polymer substrate [13], [14], [18] such as polyethersulfone (PES) or polyethylene terephthalate (PET). The advantages of this method include the merit of transition metal oxides which have thoroughly investigated for RRAM due to the high resistance ratio and chemical/mechanical endurance as well as the compatibility with Si-based device process. However, this method cannot be the ultimate solution suitable to the concept of flexible RRAM by changing the intrinsic property, but just the roundabout way to deposition of very thin transition metal oxide film onto flexible substrate. The other is to use a flexible polymer which possesses resistance switching capability [15]–[17]. However, the reported results using polymers capable of resistance switching usually exhibited severe problems such as rather poor performance and complex molecular structure requiring highly complicated synthesis and extremely low yield. Therefore, it would be highly challenging to meet the requirements for practical device fabrication.

To suggest promising alternative to realize the flexible RRAM instead of the above-mentioned ways, we focused on the mechanism of unipolar resistance switching (URS), which includes formation and rupture of conductive path in insulating matrix [8], [20]. A material capable of showing switching behavior under URS mode can be treated as a system which has two independent components; the one is a resistance switching filament showing the conductivity varying capability, which carries out the on/off switching operation through rupture and formation of conductive path, and the other is a dielectric matrix (Fig. 1). In the light of these facts, we propose to use one dimensional resistance switching filler (RS filler) to provide a current pathway depending on applied voltage and its hybridization with flexible dielectric matrix to construct a resistance switching nanocomposite of flexibility. In other words, a nanocomposite, consisted with RS filler and dielectric matrix, can obtain resistance

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W. Jeon is with the Department of Materials Science and Engineering, Dankook University, Cheonan 31116, South Korea (e-mail: woojin.jeon@gmail.com).

Y. Kim and S.-S. Lee are with the KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 02841, South Korea, and also with the Photo-Electronic Hybrids Research Center, Korea Institute of Science and Technology, Seoul 02792, South Korea (e-mail: alwpo@kist.re.kr; s-slee@kist.re.kr).

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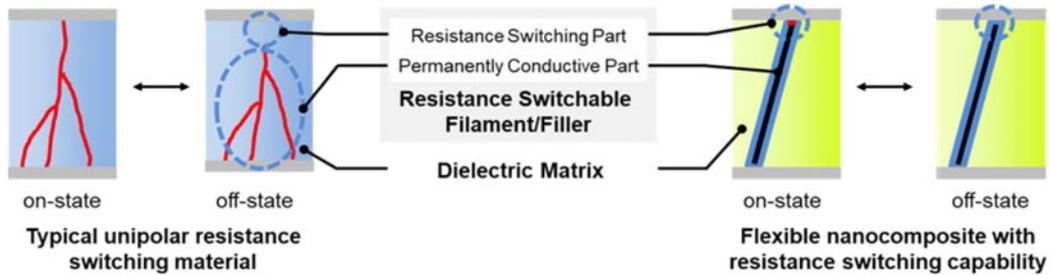


Fig. 1. Schematic diagrams of typical RRAM (left) and new concept of RRAM based on one-dimensional (1-D) resistance switchable filler (right). Rigid dielectric matrix (blue) and resistance switchable filaments (red) are replaced to flexible dielectric polymer matrix (green) and permanent resistance switchable fillers (black) composed of conductive 1-D fillers wrapped with  $\text{TiO}_2$  passivation layer (blue for HRS, red for LRS), respectively.

switching property and flexibility, simultaneously, from RS filler and dielectric matrix, respectively. At this point, one dimensional resistance switching fillers are composed of two components; the one is permanently conductive core providing facile electron transport, and the other is a skin layer to gate the electron flow delivered through the conductive core. When embedded in polymer matrix, fillers of one-dimensional shape above percolation limit tend to form a highly connected network-like structure which can contribute as deformable pathways for electron transfer (Fig. 1).

Recently, a novel hybrid system employing conformal passivation layer of crystalline  $\text{TiO}_2$  on Ag nanowires has been proposed to form a polymer nanocomposite exhibiting an excellent resistance switching performance [19]. Furthermore, it was also found that the switching performance could be enhanced with longer nanowires. However, it has been well known that Ag nanowire demonstrates conductivity instability induced by oxidative degradation and molecular migration, and also tends to show easily mechanical failure which is not suitable in preparing a flexible nanocomposite. Moreover, investigation for revealing exact mechanism for resistance switching characteristics of polymer nanocomposite was not sufficient. To fulfill our intention, in this study, alternative one dimensional (1-D) nano-sized conductive materials such as carbon nanotube (CNT) and carbon nanofiber (CNF) with high aspect ratio, mechanical flexibility, and outstanding electron conductivity have been chosen to be passivated with transition metal oxide layer such as  $\text{TiO}_2$ , and embedded in a dielectric matrix (equivalence of insulating matrix of typical URS materials) to form a nanocomposite. As described in Fig. 1, if 1-D nanocarbon fillers would be distributed in a dielectric matrix to form a conductive path, and the passivation layer wrapping the 1-D nanocarbon could gate electron flow between the nanotube junctions, the resistance of the whole nanocomposite would be determined by the resistance switchable component wrapping the 1-D fillers, and accordingly, the nanocomposite could attain resistance switching capability.

## II. EXPERIMENT

### A. Preparation of RS Fillers From CNT ( $\text{CNT-TiO}_2$ ) and Carbon Nanofiber ( $\text{CNF-TiO}_2$ )

Acid-treated single-walled carbon nanotube (SWCNT, Hanwha Nanotech) of 10 mg was dispersed in mixture of dimethylformamide (DMF, Aldrich) of 10 mL, deionized water

of 17 mL, and  $\text{TiCl}_4$  (diluted to 2 M, Merck) of 10 mL. The resulted suspension was heated at  $60^\circ\text{C}$  for 8 h for 20 nm-thick  $\text{TiO}_2$  coating on the surface of SWCNT, yielding grayish precipitates. The crude product was collected by filtration, followed by deionized water rinsing to remove by-products (HCl). Subsequently, the SWCNT coated with  $\text{TiO}_2$  (SWCNT- $\text{TiO}_2$ ) was dried by using a freeze dryer for 24 h.

Vapor-grown carbon nanofibers (CNF, diameter about 100 nm, Showa Denko) were treated with concentrated acid solution for surface modification; as-received CNF was suspended in a 3:1 (v/v) mixture of  $\text{H}_2\text{SO}_4$  (98 %) and  $\text{HNO}_3$  (68 %), and the suspension was ultrasonicated in a bath-type sonicator for 24 h at room temperature, followed by refluxing at  $200^\circ\text{C}$  for 2 h. The suspension was washed with distilled water to show pH 7, and freeze-dried for 24 h. The pre-treated CNF of 10 mg was added to the solution of deionized water of 20 mL containing  $\text{TiCl}_4$  (2M) of 10 mL. The remaining processes for preparing CNF coated with  $\text{TiO}_2$  (CNF- $\text{TiO}_2$ ) were the same as described for the preparation of the RS fillers based on SWCNT.

### B. Preparation of Nanocomposite

All the RS fillers synthesized as above were heat-treated in a tubular furnace programmed at  $100^\circ\text{C}$  for 1 h and then at  $400^\circ\text{C}$  for 1 h under ambient atmosphere to induce crystallization of  $\text{TiO}_2$  component. The heat-treated RS fillers were mixed with monomeric epoxy (UME-305, Kukdo Chemical) using a high-speed paste mixer. The content of each RS filler in epoxy was fixed at 1.0 wt.%, which is far beyond percolation threshold [21]. A test cell for measuring resistance switching characteristics was prepared as follows; A 100 nm-thick Pt was sputtered on glass substrate to form a bottom electrode (BE). The epoxy pastes containing RS fillers were cast on the Pt-sputtered glass substrate, followed by the thermal treatment at  $130^\circ\text{C}$  for 3 h to cure epoxy component to form a RS filler/epoxy nanocomposite film with thickness of about  $10\ \mu\text{m}$ . Finally, a rectangular-shaped Ag spot with area of  $2.0 \times 2.0\ \text{mm}^2$  as top electrode (TE), was formed on the composite film, resulting in a stack of MIM structure of Pt(BE)/RS filler-epoxy composite/Ag(TE). For the bending test, Pt sputtered PET film was employed as a substrate instead of glass. RS filler was mixed with 10 wt.% PVA solution ( $M_w \approx 50,000\ \text{g/mol}$ ) diluted with deionized water, and then the mixture was stirred at  $70^\circ\text{C}$  for 6 h. After that, the mixed solution containing the RS filler was spin-coated on the Pt/PET

substrate, followed by solvent removal at 70 °C for 24 h in an oven. The content of RS filler in RS filler-PVA composite was 1.0 wt.%. Top electrode was defined by same manner as described in preparation for MIM structure of Pt(BE)/RS filler-epoxy composite/Ag(TE).

### C. Characterizations

The RS filler/epoxy nanocomposites were subjected to current-voltage (I-V) measurements (Parstat 2273, Princeton Applied Research) at room temperature under ambient conditions. Morphological analyses were performed on field-emission scanning electron microscope (FE-SEM, Jeol JSM-6701F) operated at 15 kV. UV-Vis measurements were made on Jasco V-670 spectrophotometer. X-ray diffraction (XRD) measurements were performed on Bruker D8 Discover running at 18 kW and the target was Cu standard ( $\lambda = 0.15405$  nm). Scanning was performed at a rate of 3 degree/min. For correction of scattering angle, a pure silicone standard was used.

## III. RESULTS & DISCUSSION

It has been understood that the URS behavior would come from filamentary conduction paths, of which formation and rupture are believed to be governed by applied electric field and Joule heating, respectively [22]. However, its microscopic origin and the filaments themselves have not been clearly identified and they remain controversial so far. Furthermore, there would be a limit in memory design, since it is hard to meet a reproducible formation of conductive path through film thickness. Instead of forming a fugitive conductive path by charge migration, one dimensional conductive materials providing conductive path across the polymer matrix with high conductivity are suggested to be coated with field-responsive dielectric components to form RS fillers.

First, we prepared RS fillers of core-shell structure; core of SWCNT and shell region of  $\text{TiO}_2$  which has been well known to exhibit the electric field-driven resistance switching behavior [13], [19], [22]–[29]. As found in Fig. 2(a), the microstructure of SWCNT- $\text{TiO}_2$  examined by FE-SEM showed that the surface of nanotube was roughly coated by  $\text{TiO}_2$ , of which crystal structure was the anatase phase confirmed by XRD (Fig. 3). In I-V measurements, while the neat epoxy exhibited the typical I-V curve of insulator as shown in Fig. 2(b), the unipolar resistance switching behavior was observed for the SWCNT- $\text{TiO}_2$  embedded epoxy composite [Fig. 2(c)], of which the resistance ratio  $R_{\text{off}}/R_{\text{on}}$  reached to almost  $\sim 10$  [Fig. 2(d)], implying that a dielectric polymer was dramatically transformed to a resistance switching-capable material due to the presence of SWCNT- $\text{TiO}_2$ . To scrutinize the origin of the resistance switching behavior in the epoxy composite, I-V measurements for epoxy composites containing either  $\text{TiO}_2$  particles or pristine SWCNT alone were conducted, respectively. In case of the composite employing neat  $\text{TiO}_2$  alone [Fig. 4(a)], the I-V curve was found highly similar to that of neat epoxy, demonstrating that no conductive path across the matrix was developed, even after  $\text{TiO}_2$  particles of 10 wt.% were introduced. In case of the composite

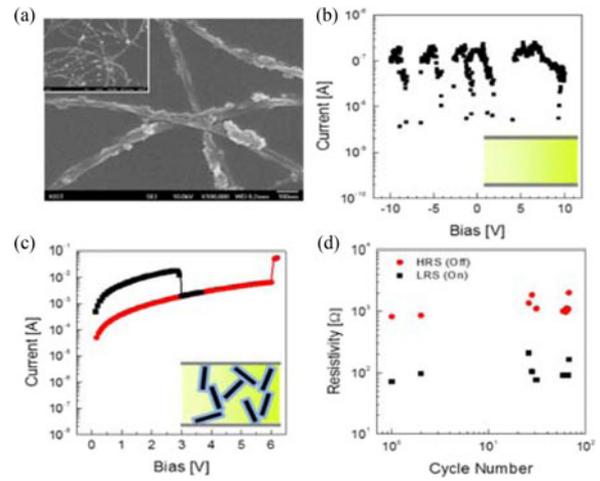


Fig. 2. The results of CNT-  $\text{TiO}_2$ /epoxy nanocomposite: (a) microstructure of CNT-  $\text{TiO}_2$  examined by FE-SEM shows SWCNT coated with  $\text{TiO}_2$ . (b) I-V curve exhibits that neat epoxy is a typical insulator with no current path, represented schematically as the inset. (c) I-V curve of CNT-  $\text{TiO}_2$ /epoxy composite shows the resistance switching behavior. The inset figure is the schematic representation of suggested current path formed with CNT-  $\text{TiO}_2$  (the SWCNT core in black with the blue-colored  $\text{TiO}_2$  phase) in epoxy matrix (described in green). (d) The cyclic test shows that the resistance ratio of the CNT-  $\text{TiO}_2$ /epoxy composite is preserved at the level of one order.

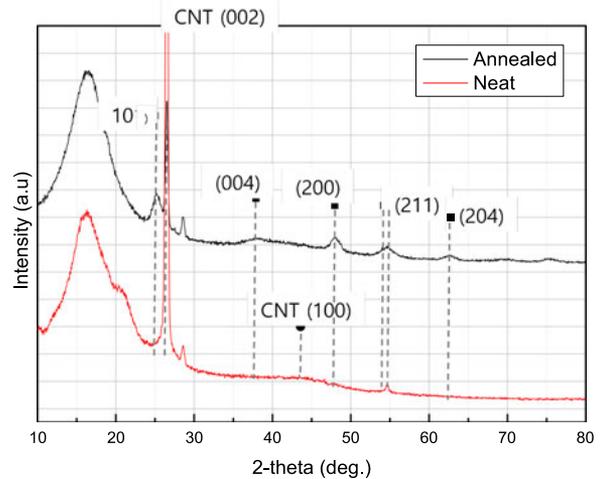


Fig. 3. XRD spectra of SWCNT- $\text{TiO}_2$  evidencing the presence of anatase structure of  $\text{TiO}_2$  component.

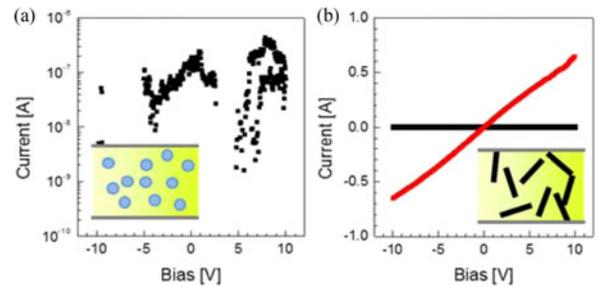


Fig. 4. (a)  $\text{TiO}_2$ /epoxy composite shows the same I-V characteristics as that of neat epoxy. It is presumed that  $\text{TiO}_2$  particles are isolated in epoxy matrix so that it cannot make current path, described as the inset figure. (b) SWCNTs of 0.05 wt% (black line) or 1 wt% (red line) don't exhibit any trace of the RS behavior but the linear I-V curve over the scanned voltage range.

employing pristine SWCNT alone, while the resistance switching behavior by SWCNT has been reported by other groups [30]–[32], there was no obvious evidence concerning a large resistance change by electric field to refer resistance switching behavior in our study; instead, as shown in Fig. 4(b), the I-V curve just showed percolation behavior of SWCNT in terms of the concentration, probably due to that the resistance switching behavior would be too small to be detected under the experimental detection limit. Therefore, it could be concluded that the TiO<sub>2</sub>-coated SWCNT successfully imparts resistance switching capability to the nanocomposite.

However, it was also found that SWCNT-TiO<sub>2</sub>/epoxy nanocomposite has a shortcoming impeding the application as resistance switching material; the R<sub>off</sub>/R<sub>on</sub> ratio is not enough to ensure the usability as memory device. Furthermore, the switching behavior was not well reproducible; the reset (switching from low resistance state (LRS, on-state) to high resistance state (HRS, off-state)) was relatively facile, but the set (switching from HRS to LRS) occurred poorly. The reason of this odd behavior is supposed to be correlated with that the electron conduction across the TiO<sub>2</sub> layer is not sufficient, since the voltage drop by SWCNT would be high due to its structural imperfection of sp<sup>2</sup> graphitic lattices, possibly induced by the chemical treatment of SWCNT for the debundling and distribution control [33], [34]. Another possible reason would be the structural imperfection of TiO<sub>2</sub> layer; SWCNT for conductive path should be well wrapped by TiO<sub>2</sub> layer, and any void or structural defect in TiO<sub>2</sub> layer would cause electron leakage impeding the switching behavior. As found in Fig. 2(a), it would be hard to say that the TiO<sub>2</sub> components have evenly adhered on SWCNT. Unfortunately, an extremely perfect SWCNT without any defects, even though it cannot be isolated without chemical or physical damages in terms of practical point of view, cannot afford to provide robust anchoring sites to the TiO<sub>2</sub> components due to its hydrophobic surface nature, and thus, the TiO<sub>2</sub> moieties would easily tend to aggregate rather than to spread for even adhesion on SWCNT, resulting in incomplete formation of passivation layer. Therefore, it has been tried to replace the conductive component of RS filler from SWCNT to another material capable of showing higher surface compatibility with TiO<sub>2</sub> and electron mobility comparable to that of SWCNT, and thus, one of SWCNT's relatives, CNF was chosen as a conductive core of the RS filler alternative, CNF-TiO<sub>2</sub>. The structure of each CNF could be presumed as a fully filled that of SWCNT, and thus, even if CNF surfaces are subjected to severe chemical oxidation reaction to induce large amount of functional groups which play a role of anchoring site to TiO<sub>2</sub> passivation layer, the sub-surface sp<sup>2</sup> graphitic region of pre-treated CNF would retain conductive nature similar to that of pristine CNF. CNF also has less hydrophobic surface chemistry than that of SWCNT. Fig. 5(a) and (b) show that the surface of CNF is well passivated by TiO<sub>2</sub> (CNF-TiO<sub>2</sub>), and the rod-like morphology of high aspect ratio is preserved. CNF-TiO<sub>2</sub> was mixed with epoxy as polymer matrix (CNF-TiO<sub>2</sub>/epoxy nanocomposite), which was subjected to tests for the switching behavior. The I-V curves for the nanocomposite containing 1.0 wt.% of CNF-TiO<sub>2</sub> showed the R<sub>off</sub>/R<sub>on</sub> of up to ~10<sup>4</sup>,

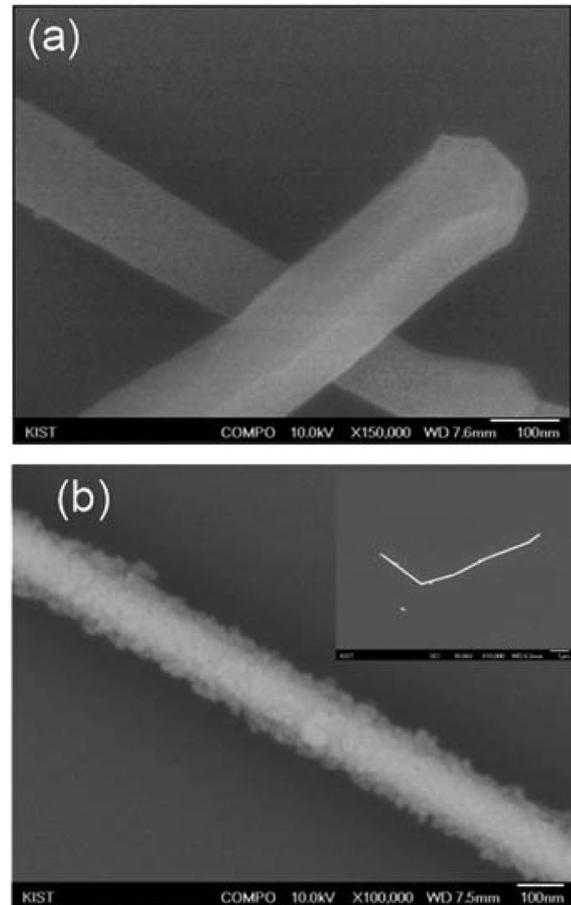


Fig. 5. SEM images of (a) pristine CNF and (b) CNF-TiO<sub>2</sub> which show that the CNF surface was well coated with TiO<sub>2</sub> component.

which is as equivalent as reported results of TiO<sub>2</sub>-only thin film [13], [23]–[25], [27], and a reversible RS behavior including “set” and “reset” process [Fig. 6(a)]. Furthermore, as shown in Fig. 6(b)–(d), the nanocomposite exhibited very reproducible resistance switching behavior over 300 cycles of the I-V sweeps without any switching failure. More statistical exploring on the set and reset voltages can be seen in Fig. 6(d), where they are  $2.53 \pm 0.11$  and  $3.43 \pm 0.11$  V, respectively, demonstrating a reliable switching behavior with small dispersion. The cumulative distribution of the set and reset voltages estimated with more than 100 test devices shows the values were  $2.54 \pm 0.14$  and  $3.44 \pm 0.12$  V, respectively, demonstrating extremely low device-to-device variability, as found in Fig. 6(e).

To clarify the resistance switching mechanism in the CNF-TiO<sub>2</sub>/epoxy nanocomposite, the temperature coefficient of resistance (TCR) of the nanocomposite film, and resistance switching behavior with respect to the compliance current were evaluated in the LRS. TCR evaluation was performed based on the following equation:

$$R_T = R_o [1 + \alpha (T - T_o)] \quad (1)$$

where  $\alpha$ ,  $R_o$ , and  $R_T$  are the TCR value, the resistance of the LRS at the initial temperature  $T_o$ , and the resistance of the LRS at temperature  $T$ , respectively. When the temperature ( $T$ ) range

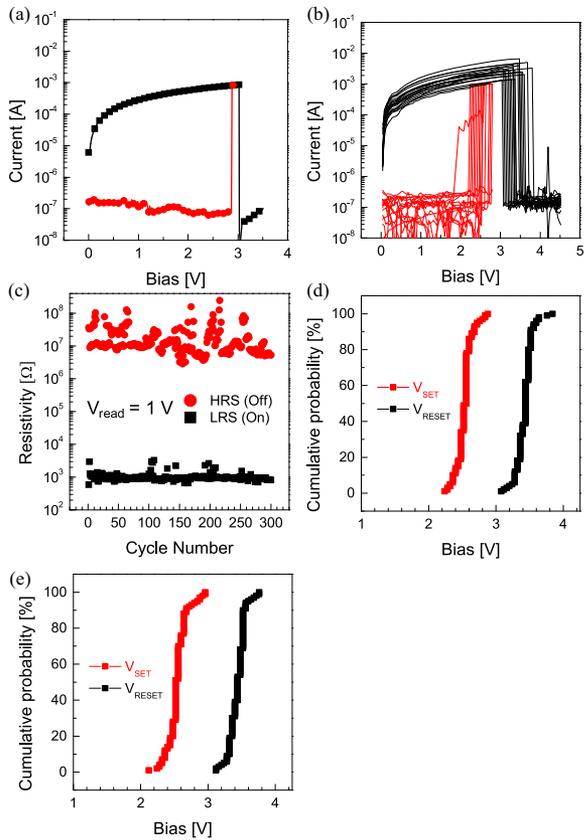


Fig. 6. I-V curves for (a) CNF-TiO<sub>2</sub>/epoxy composite, (b) I-V curves of the composite with CNF-TiO<sub>2</sub> RS filler for the I-V sweep of 300 cycles. (c) The resistance of LRS and HRS of the sample in I-V sweep. (d) Cumulative plot of the set and reset voltages measured in Fig. 6(b). (e) Cumulative plot of the set and reset voltages for 100 test devices.

for the I-V measurements was from 303 to 343 K, the calculated  $\alpha$  values of the MIM was  $2.29 \times 10^{-5} \text{ K}^{-1}$  [Fig. 7(a)]. This value is comparable to the reported value of the Magnéli phase (mostly Ti<sub>4</sub>O<sub>7</sub>,  $1.48 \times 10^{-5} \text{ K}^{-1}$ ), implying that the resistance switching behavior of the nanocomposite is attributed to the Magnéli-phase conductive filament mechanism of the TiO<sub>2</sub>. I-V curves with respect to compliance current ( $I_{cc}$ ) were observed as depicted in Fig. 7(b). Current level of LRS is decreased with decreased  $I_{cc}$  from 1 mA to 0.1 mA. It is hard to observe proper resistance switching behavior in case of  $I_{cc}$  of 0.01 mA. This result is well consisted with that lower  $I_{cc}$  induces narrower filament, resulting lower current level in LRS [35]. Retention properties employing  $I_{cc}$  of 1 mA and 0.1 mA, were also examined [Fig. 7(c)], and it was found that the retention of both LRS and HRS for  $I_{cc}$  of 1 mA and 0.1 mA were also confirmed up to  $10^5$  s. About the fact that the CNF-TiO<sub>2</sub> showed the switching performance superior to that of the SWCNT-TiO<sub>2</sub>, it could be speculated that the switching behavior would be strongly related with the differences between CNF and SWCNT in terms of the physical structure; First, on the physical structural point of view, while SWCNT was wrapped with speckled TiO<sub>2</sub> layer in swirled shape, CNF-TiO<sub>2</sub> showed a highly conformal TiO<sub>2</sub> coating layer along with a long rod-like morphology [Fig. 5(b)], of which structures would be favorable to provide an ideal

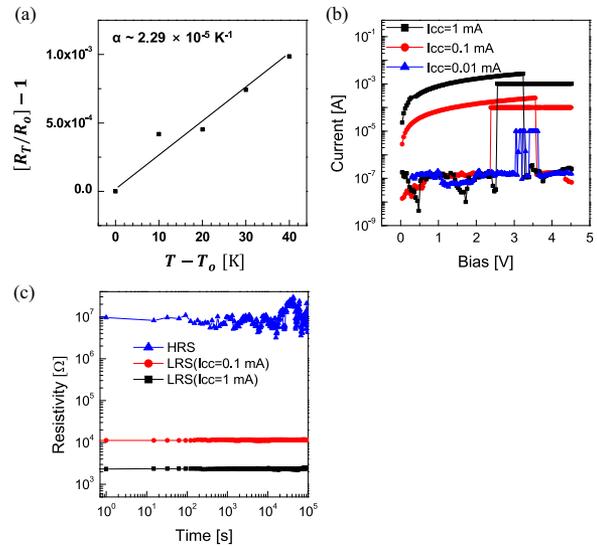


Fig. 7. (a) Temperature coefficient of resistance curve of Ag-TiO<sub>2</sub>-CNF system. (b) I-V curves of the composite containing the CNF-TiO<sub>2</sub> RS filler of 1 wt.% when varying the compliance current ( $I_{cc}$ ). (c) The result of retention test at the temperature of 278 K.

resistance switchable current path between the top and bottom electrodes. Also, the intrinsic electrical property would be another important governing factor. If the conductivity of core component of RS filler is not high, the applied electric field across TiO<sub>2</sub> passivation layer would be inadequate to operate resistance switching behavior since the voltage drop by conductive component would be high. Actually, the electrical conductivities of pre-treated CNF and acid-treated SWCNT used in this work were  $1.44 \times 10^4$  and  $2.03 \text{ S/cm}$ , respectively, when examined as a buckypaper form under four-point probe measurement.

Finally, to examine the response of switching behavior under mechanical deformation, the CNF-TiO<sub>2</sub> fillers were mixed with a flexible polymer, PVA which replaces epoxy of dielectric matrix, and the I-V characteristics collected from the CNF-TiO<sub>2</sub>/PVA nanocomposite were compared before and after bending stress of up to 4,000 cycles with bending radius of 3 mm, as shown in Fig. 8. One thing to note is that there was no notable change in the switching behavior when subject to mechanical deformation, implying that the combination of deformable network structure of CNF-TiO<sub>2</sub> and flexible dielectric matrix is seemingly successful to provide the flexible nanocomposite exhibiting resistance switching behavior. This notable performance stability under mechanical stress would be related with the presence of the physical interaction such as hydrogen bonding between the CNF-TiO<sub>2</sub> and PVA as well as the inherent elastic mechanical properties originating from the network structure of one-dimensional components [36].

It is believed that there is a need for further improvement, such as increasing switching speed and reliability via the use of appropriate material of which switching performance is tunable by control of thickness and structural imperfection of passivation layers and the distribution of RS fillers. However, it should be noted that the concept of using TiO<sub>2</sub>-wrapped conductive component of one dimensional structure as resistance

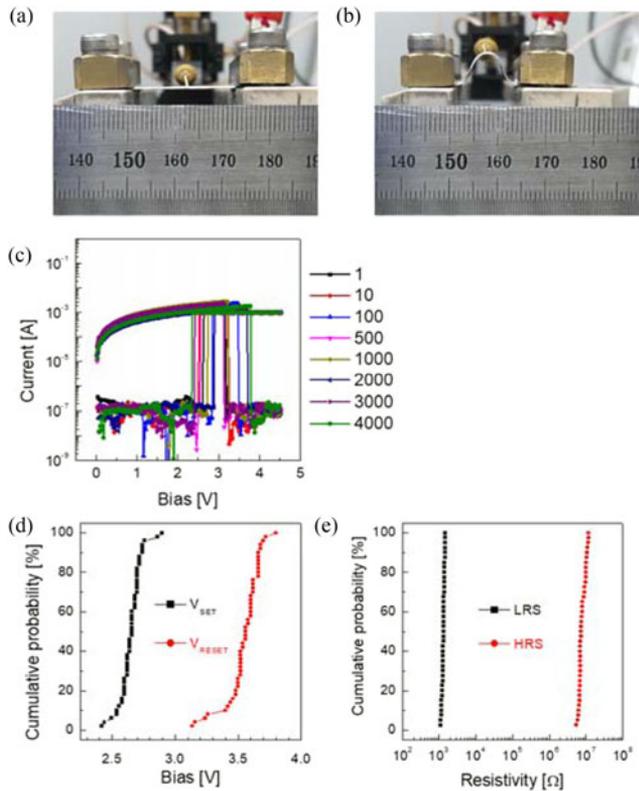


Fig. 8. Photographs of the samples in the bending test (a) in flat and (b) with bending radius of 3 mm. (c) I-V curves measured after the bending of 1 to 4000 cycles. Cumulative probability plot of (d) operating voltage, and (e) resistance of LRS and HRS from I-V curves of Fig. 8(c).

switching medium performed well, even in a non-optimized state. The advantages of our approach include cheap and simple fabrication procedures along with sustainable performances suitable to RRAM application.

#### IV. CONCLUSION

We have successfully demonstrated a reproducible resistance switching behavior, using the simple mixture of  $\text{TiO}_2$ -wrapped 1-D nanocarbons and dielectric polymer matrix. The 1-D conductive nanocarbon fillers such as SWCNT or CNF were wrapped with  $\text{TiO}_2$  conformal passivation layer, and embedded in dielectric polymer matrix to form network-like distribution, which successfully exhibited reproducible resistance switching behavior of high on/off ratio. It is notable that the perfect formation of conformal passivation layer on conductive components significantly alters the switching performance.

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**Woojin Jeon** received the Bachelor's and M.Sc. degrees in materials science and engineering from the Korea Advanced Institute of Science and Technology, Daejeon, South Korea, in 2005 and 2007, respectively, and the Ph.D. degree in materials science and engineering from Seoul National University, Seoul, South Korea, in 2015. He then joined the Samsung Advanced Institute of Technology as a Technical Staff member in 2015. He was a Postdoctoral Research Fellow with the Grenoble Alpes University, National Center for Scientific Research, Grenoble, France, in

2017. He is currently an Assistant Professor with the Department of Materials Science and Engineering, Dankook University, Yongin, South Korea. His research focuses on the electrical and chemical properties of high-*k* materials and novel metal electrode of the metal-insulator-metal structures, and the device physics especially on dielectric and interface between dielectric and metal. His current research interest focuses on the deposition process evaluation with ALD, CVD for the next-generation semiconductor applications.



**Youngjin Kim** received the Bachelor's and M.Sc. degrees in chemical engineering from Kyonggi University, Suwon, South Korea, in 2010 and 2012, respectively. He is currently working toward the Ph.D. degree in NBIT convergence at the KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul, South Korea. From 2012 to 2013, he was a Research Scientist with the Korea Institute of Science and Technology, Seoul, South Korea. His research focuses on the phenomenon of ion transport in the electrolyte of dye-sensitized solar cells and the insulating medium of the MIM structures. His current research interests include physical and electrical characterization of MIM structures for resistive RAMs and neuromorphic devices.



**Sang-Soo Lee** received the B.S. and Ph.D. degrees in chemical technology from Seoul National University, Seoul, South Korea, in 1990 and 1995, respectively. He was a Research Fellow with the Material Science and Engineering, University of Michigan, Ann Arbor, MI, USA, from 1995 to 1997. He then joined the functional nanocomposite division, Korea Institute of Science and Technology, Seoul, South Korea, where he is currently the Head of the Photo-Electronic Hybrids Research Center. His research interests include interface chemistry, materials science, and electrical engineering. Especially, his work focuses on the development of novel hybrid materials and devices for the electron/ion transport-based interconnection and the renewable energy conversion. He also serves as an Associate Editor for the *Macromolecular Research*.