

# Multilevel characteristics of TiO<sub>x</sub> transparent non-volatile resistive switching device by embedding SiO<sub>2</sub> nanoparticles

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## Research Article

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# Abstract

TiO<sub>x</sub>-based resistive switching devices have recently attracted attention as a promising candidate for next-generation non-volatile memory devices. A number of studies have attempted to increase the structural density of resistive switching devices. The fabrication of a multi-level switching device is a feasible method for increasing the density of the memory cell. Herein, we attempt to obtain a non-volatile multi-level switching memory device that is highly transparent by embedding SiO<sub>2</sub> nanoparticles (NPs) into the TiO<sub>x</sub> matrix (TiO<sub>x</sub>@SiO<sub>2</sub> NPs). The fully transparent resistive switching device is fabricated with an ITO/TiO<sub>x</sub>@SiO<sub>2</sub> NPs/ITO structure on glass substrate, and it shows transmittance over 95 % in the visible range. The TiO<sub>x</sub>@SiO<sub>2</sub> NPs device shows outstanding switching characteristics, such as a high on/off ratio, long retention time, good endurance, and distinguishable multi-level switching. To understand multi-level switching characteristics by adjusting the set voltages, we analyze the switching mechanism in each resistive state. This method represents a promising approach for high-performance non-volatile multi-level memory applications.

## Introduction

The resistive switching device has attracted attention as a promising candidate for next-generation non-volatile memory devices, as it can be used to achieve low power consumption, good storage capability, high-speed operation, and stable switching properties.<sup>1-4</sup> Many kinds of inorganic transitional metal oxide materials have been proposed for the active layer, including TiO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, HfO<sub>2</sub>, and NiO.<sup>5-8</sup> Among them, TiO<sub>2</sub> has been widely studied due to its fast switching speed and promising performance, as well as intrinsic variety of possible crystal phases, and the associated richness of its switching dynamics.<sup>9-11</sup> Recently, scaling down the device size and increasing the structural density of the memory array have become highly sought after targets in resistive random access memory (ReRAM) devices. The cross-bar array architecture is a widely accepted method with structural benefits, which is sandwiched by inserting active layer between the parallel bottom electrode (BE) and perpendicular to the top electrode (TE).<sup>12-14</sup> Another aspect that has received considerable attention is the fabrication of a multi-level switching device, which can store multi-bit data in one cell and can enhance the physical density of the memory device.<sup>4,15,16</sup> In general, a resistive switching device changes electrically between a high resistive state (HRS) and a low resistive state (LRS) through the application of electrical inputs. By contrast, the multi-level switching device has various HRS or LRS; specifically, the multi-level switching characteristics can be generated by either modifying the length of the gap between the conductive filament (CF) and electrode, which is controlled by adjusting the stop voltage during the RESET process, or by controlling the diameter/density of the CF during the LRS process.<sup>17-19</sup> Recent research has indicated that the switching performance of a switching device can be improved by incorporating nanostructures into the matrix of the switching layer. Tsigkourakos et al. has reported the fabrication of a TiO<sub>2-x</sub>-based resistive switching device by embedding Pt nanocrystals, and this device achieved low power operation current and obtained multi-level switching characteristics by controlling the compliance current.<sup>20</sup> Yoon et al.

embedded Ru nanodots into  $\text{TiO}_x$  thin film to achieve resistive switching uniformity among  $\text{TiO}_2$  memory cells.<sup>21</sup> The embedment of metal nanostructures has attracted substantial attention, as it improves the resistive switching performance by controlling the size and shape. However, metal nanostructure-embedded switching device has a crucial issue for fabrication of transparent switching devices, due to the inherent opaqueness of metal; this means it is unfeasible to use such devices in next-generation memory devices. Transparent memory devices are extremely useful due to their potential applications in the field of transparent electronics. Herein, we attempt to achieve fully transparent non-volatile memory devices, as well as multi-level switching characteristics, by using  $\text{SiO}_2$  nanoparticles (NPs).

In this study, we prepared a multi-level switching device with transparent characteristics by embedding  $\text{SiO}_2$  NPs into the  $\text{TiO}_x$  matrix (structure with ITO/ $\text{SiO}_2$  NPs-embedded  $\text{TiO}_x$ /ITO) on glass substrate using a solution process. The  $\text{SiO}_2$  NPs-embedded  $\text{TiO}_x$  device showed high transmittance as well as outstanding electrical performance, including a large on/off current ratio, long retention time, good endurance, and multi-switching characteristics.

## Results And Discussion

Figure 1 (a) and (b) show the surface morphologies of the  $\text{TiO}_x$  and  $\text{TiO}_x@ \text{SiO}_2$  NPs films, which were obtained using atomic force microscopy (AFM) measurement. It can clearly be seen that the nanoparticles with a sphere shape are well embedded into the  $\text{TiO}_x$  matrix. In addition, the root-mean-square (RMS) roughness values for  $\text{TiO}_x$  and  $\text{TiO}_x@ \text{SiO}_2$  NPs are changed from 0.42 to 2.95 nm, respectively. Further, the average height of  $\text{SiO}_2$  NPs is approximately 20.61 nm, as shown in Fig. 1 (c). Moreover, TEM measurement was conducted to examine the cross-sectional structures of the  $\text{TiO}_x$  and  $\text{TiO}_x@ \text{SiO}_2$  NPs switching devices. As shown in Fig. 1 (d) and (e), the TEM image of the  $\text{TiO}_x$  device clearly shows stacking of ITO/ $\text{TiO}_x$ /ITO. On the other hand, the brighter areas with a spherical shape that are well distributed in the region of the  $\text{TiO}_x@ \text{SiO}_2$  NPs layer are estimated to be  $\text{SiO}_2$  NPs. For a detailed analysis of the bright areas in the  $\text{TiO}_x@ \text{SiO}_2$  NPs layer, high-angle annular dark-field scanning TEM (HAADF-STEM) was taken across the  $\text{TiO}_x$  and  $\text{TiO}_x@ \text{SiO}_2$  NPs, as shown in Fig. 1 (f) and (j). According to HAADF-STEM, the heavy element shows bright contrast, while the light element shows dark contrast.<sup>22</sup> In the HAADF-STEM image of  $\text{TiO}_x@ \text{SiO}_2$  NPs, the darker region that exists in the shape of a sphere in the  $\text{TiO}_x$  matrix corresponds to  $\text{SiO}_2$  NPs. To investigate the chemical species, EDS spectra are taken. In Fig. 1 (g), (h), and (i), only Ti and O elements are detected in the case of the  $\text{TiO}_x$  device, whereas the  $\text{TiO}_x@ \text{SiO}_2$  NPs device is composed of Ti, O, and Si as shown in Fig. 1 (k), (l), and (m). Based on the cross-sectional information, the distribution of  $\text{SiO}_2$  NPs in  $\text{TiO}_x$  is definitively confirmed.

Figure 2 (a) shows the transmittances of the ITO/ $\text{TiO}_x$ /ITO device and the ITO/ $\text{TiO}_x@ \text{SiO}_2$  NPs/ITO structures. As shown in the inset in the Fig. 2 (a), the two devices are both highly transparent. To compare the optical transmittances values of the  $\text{TiO}_x$  and  $\text{TiO}_x@ \text{SiO}_2$  NPs devices, we measured the optical transmittance in the visible range from 400 to 800 nm, and we ultimately obtained respective values of

87 and 95 %. It is concluded that the optical transmittance is improved by embedding SiO<sub>2</sub> NPs into TiO<sub>x</sub>. Figure 2 (b) shows the refractive index and extinction coefficient of TiO<sub>x</sub> and TiO<sub>x</sub>@SiO<sub>2</sub> NPs, which were obtained using a four-phase model comprising glass substrate, ITO layer, TiO<sub>x</sub> layer, and ambient layer.<sup>23</sup> For the TiO<sub>x</sub> film, the refractive index was 1.96, which is smaller than that of conventional TiO<sub>2</sub> film (which ranges from 2.4 to 2.75 at 550 nm).<sup>24</sup> As research has shown that the refractive index can be related to the film density, we consider that a decrease in the refractive index for the prepared TiO<sub>x</sub> film implies a lower density than that of conventional TiO<sub>2</sub> film.<sup>25,26</sup> In the TiO<sub>x</sub>@SiO<sub>2</sub> NPs, the value of the refractive index decreases to 1.72, as it is affected by the embedment of the small refractive index of SiO<sub>2</sub> NPs (~ 1.47).<sup>27</sup> Embedding SiO<sub>2</sub> NPs into the TiO<sub>x</sub> matrix also leads to a decrease in the extinction coefficient, which represents a decrease in absorption. The optical band gap can be extracted by extrapolating the linear portion of the extinction coefficient. The optical band gap of TiO<sub>x</sub> and TiO<sub>x</sub>@SiO<sub>2</sub> NPs is found to be 3.70 and 3.75 eV, respectively. These values are consistent with the TiO<sub>x</sub> films made by the solution process, and the TiO<sub>x</sub> and TiO<sub>x</sub>@SiO<sub>2</sub> NPs are both completely transparent in the visible region.<sup>28</sup>

Figure 3 (a) – (e) respectively show the Ti 2*p*, O 1*s*, and Si 2*p* core-level spectra of the TiO<sub>x</sub> and TiO<sub>x</sub>@SiO<sub>2</sub> NPs films. The XPS analysis was conducted after surface sputtering for 10 s to eliminate the carbon contamination, which was performed by Ar sputtering at 500 W. The survey spectra were measured to acquire accurate compositions of the TiO<sub>x</sub> and TiO<sub>x</sub>@SiO<sub>2</sub> NPs films (Figure S1). In the case of TiO<sub>x</sub>@SiO<sub>2</sub> NPs, the TiO<sub>x</sub> matrix consists of 11.5 % Si. To elucidate the chemical bonding states, the core-level spectra of Ti 2*p*, O 1*s*, and Si 2*p* were normalized, then deconvoluted into Gaussian peaks. Figure 3 (a) and c show the Ti 2*p* spectra, wherein the two peaks centered at 459.15 and 453.45 eV can be attributed to Ti 2*p*<sub>1/2</sub> and Ti 2*p*<sub>3/2</sub>, respectively. The separation between these two peaks is calculated to be ~ 5.7 eV, which suggests the existence of Ti<sup>4+</sup> oxidation states in the TiO<sub>2</sub>.<sup>29</sup> The shoulder peaks at 458.15 and 452.45 eV can be correlated with the Ti<sup>3+</sup> oxygen deficient states in TiO<sub>x</sub>, which originate from the reduction of Ti<sup>4+</sup> by free electrons donated by oxygen vacancies.<sup>28,30</sup> In the TiO<sub>x</sub>@SiO<sub>2</sub> NPs, the intensity of the Ti<sup>3+</sup> peaks slightly increases relative to those of the TiO<sub>x</sub>, which is attributed to the TiO<sub>x</sub>@SiO<sub>2</sub> NPs sample having more oxygen deficient state in the TiO<sub>x</sub> matrix. The O 1*s* peaks are composed of three Gaussian peaks corresponding to the Ti–O bonds at 531 ± 0.2 eV (O1), oxygen deficient states at 532 ± 0.2 eV (O2), and hydroxyl groups at 533 ± 0.2 eV (O3), respectively, as shown in Fig. 3 (b) and (d).<sup>31</sup> Upon embedding the SiO<sub>2</sub> NPs into the TiO<sub>x</sub> matrix, the O2 peak of the TiO<sub>x</sub>@SiO<sub>2</sub> NPs drastically increases compared to those of the TiO<sub>x</sub>. There is also an increase in the O3 peak, which is associated with an increased number of residual surface hydroxyl groups; however, this is disputable, because the binding energies of the Si–O bonds overlap the hydroxyl groups attributed to O3.<sup>32</sup> In our explanation, the effect of the surface hydroxyl groups is negligible, because the dominating mechanism for the TiO<sub>x</sub>-based switching device comes from the oxygen vacancies. Si 2*p* is composed of regular SiO<sub>2</sub> (Si<sup>4+</sup>) as well as a substantial amount of oxygen deficient states in SiO<sub>x</sub> (Si<sup>3+</sup>), as shown in Fig. 3 (e).<sup>33</sup>

This indicates that the  $\text{TiO}_x@SiO_2$  NPs has a higher composition of oxygen vacancies than  $\text{TiO}_x$ . These results can be attributed to the migration of oxygen ions from the  $\text{TiO}_x$  matrix into  $SiO_2$  NPs, which is caused by the higher bond dissociation energy of Si–O ( $799.6 \pm 13.4$  kJ/mol) than that of Ti–O ( $666.5 \pm 5.6$  kJ/mol); therefore, the embedment of  $SiO_2$  NPs is shown to produce the oxygen deficient states in the  $\text{TiO}_x$  matrix.<sup>34</sup> In the  $\text{TiO}_x$ -based ReRAM, defects such as oxygen deficient states play an important role in the switching characteristics, which is strongly related to the migration of oxygen vacancies and the formation/rupture of the conductive path caused by the application of an external electric field.<sup>35</sup> It is also known that the physical size of the conductive filament depends on the concentration of oxygen vacancies. Thus, the size of the conductive filament for the  $\text{TiO}_x@SiO_2$  NPs is expected to be wider than that of the  $\text{TiO}_x$  device, and various electrical characteristics, such as multi-level switching, can be expected.

## Electrical characteristics

Figure 4 (a) and (b) show the typical I–V curves under voltage sweeping for the  $\text{TiO}_x$  and  $\text{TiO}_x@SiO_2$  NPs switching devices after the electroforming process (Figure S2). Initially, the  $\text{TiO}_x$ -based switching device is in HRS, because of the Schottky barrier at the interface of the electrode/ $\text{TiO}_x$ . In our device structure with ITO/ $\text{TiO}_x$ /ITO, the electron transport is limited due to the difference between the work-function of the ITO electrode ( $\sim 4.4$  eV) and  $\text{TiO}_x$  ( $\sim 3.8$  eV).<sup>[36, 37]</sup> As shown in Fig. 4 (a) and (b), both devices exhibit stable bipolar resistive switching characteristics. Regarding the  $\text{TiO}_x$  device, it switches from HRS to LRS, and the SET process is achieved by sweeping the voltage from 0 to 0.56 V. When sweeping the voltage from 0 to -0.62 V, the state changes from LRS to HRS, and the RESET process can be obtained. For the  $\text{TiO}_x@SiO_2$  NPs device, it is clearly indicated that the multi-level switching characteristics can be obtained by controlling the SET voltage. When the positive voltage sweeps from 0 to 1.2 V, the RS transits from the HRS to the lowest RS, denoted as LRS 1. Upon increasing the SET voltage to 2.2 and 3.3 V, the intermediate RS (LRS 2) and highest RS (LRS 3) can be achieved, respectively. During the negative voltage sweeps, the RS changes from LRS to HRS. From the I–V measurement under voltage sweeps, we obtain multi-level switching characteristics with four storage levels. Another interesting result is that the current level slightly decreases compared to that of the  $\text{TiO}_x$  device, meaning that the ratio of HRS/LRS is also improved. This result indicates that the  $SiO_2$  NPs act as an insulating layer. To ensure that the multi-level switching characteristics are due to the embedment of  $SiO_2$  NPs, the switching mechanism was examined as a function of the composition of  $SiO_2$  NPs, and it was found that the multi-level switching characteristics appeared slightly at the low composition of 4 % (Figure S3). Based on the I–V analysis, it can be concluded that the embedment of  $SiO_2$  NPs into the  $\text{TiO}_x$  matrix can significantly improve the resistive switching performance, such as multi-level switching, and obtain a high ratio of HRS/LRS for  $\text{TiO}_x$ -based switching devices.

To examine the stability of the device, as shown in Fig. 4 (c) and (d), the retention was studied by probing the RS changes in the HRS and LRS states for  $10^3$  s at room temperature, and measurements were

performed by separately reading the current at 0.1 V after the SET and RESET processes. The  $\text{TiO}_x$  device maintained a stable HRS/LRS ratio over  $10^2$  for  $10^3$  s. The  $\text{TiO}_x@SiO_2$  NPs device exhibits four well-defined RSs (HRS, LRS 1, LRS 2, and LRS 3), each of which is observed for  $10^3$  s. Further, to examine the endurance performance, the RS cycling test was conducted for  $10^2$  cycles after the SET and RESET processes, as shown in Fig. 4 (e) and (f). The two devices both show stable HRS/LRS ratios for  $10^2$  cycles. Specifically, in the case of the  $\text{TiO}_x@SiO_2$  NPs, multiple RSs are well defined for  $10^2$  cycles. The long retention time and high endurance indicate the high reliability and non-volatile nature of the  $\text{TiO}_x$ -based resistive switching devices.

## Switching mechanism

The conduction mechanism of the  $\text{TiO}_x$  and  $\text{TiO}_x@SiO_2$  NPs devices can be obtained by analysing the  $I$ - $V$  curves. For the  $\text{TiO}_x$  device, the fitting results for HRS suggest that the charge transport mechanism is in good agreement with a trap-controlled space charge limited conduction (SCLC), as shown in Fig. 5 (a). The  $I$ - $V$  curve consists of three regions with slopes of (1.06, 1.79, and 2.41), which respectively relate to the Ohmic region ( $I \propto V$ ) dominated by thermally generated free carriers; the Child's law region ( $I \propto V^2$ ), in which traps are filled by electrons; and the steep increase region ( $V \propto I^n$ ,  $n > 2$ ).<sup>28,38</sup> In the  $\text{TiO}_x$ -based switching device, oxygen vacancies in the  $\text{TiO}_x$  matrix serve as electron traps, and they lead to the formation or rupture of the conductive path. Therefore, the migration of oxygen vacancies is an important role in the deviation of slopes. In the high-voltage region, all traps in the  $\text{TiO}_x$  matrix are filled by electrons, then electrons flow through the conduction band of  $\text{TiO}_x$ , after which the  $\text{TiO}_x$  device achieves the SET process. For the RESET process, the slope is closer to  $\sim 1.00$ , which is attributed to the Ohmic behavior being the dominant carrier transport mechanism during the RESET process. Both the Ohmic and SCLC mechanisms are associated with the bulk controlled mechanism, meaning that the  $\text{TiO}_x$  device is properly explained by the conductive filament model. In the case of the  $\text{TiO}_x@SiO_2$  NPs device, it is important to understand the conduction mechanism of each RS. Figure 5 (b) shows the  $\log I - \log V$  plotting result of the  $\text{TiO}_x@SiO_2$  NPs device, and the carrier transport mechanism of LRS 1 also corresponds to a trap-controlled SCLC in the range from 0 to 1.28 V.<sup>39</sup> Upon further increasing the voltage above 1.28 V, the trap-controlled SCLC is not explained, due to the decreases in the fitted lines to 1.82 and 1.58. To validate the transport characteristics of the LRS 2 and LRS 3, we apply the trap-assisted tunnelling (TAT) model and Poole-Frenkel (P-F) emission, as shown in Fig. 5 (c) and (d), respectively. These conduction mechanisms are typically calculated when examining oxide materials with a high concentration of traps. The  $I$ - $V$  curve is linearly fitted by the TAT model, which describes a plot of  $\ln(I) - 1/V$ , as shown in Fig. 5 (c). The TAT is attributed to the traps, such as oxygen vacancies, which help the electrons tunnel from cathode to anode.<sup>40</sup> In the high-voltage region, the discrete trap sites are created in the switching stack, and carrier conduction becomes possible through the trap-to-trap tunnelling process. Moreover, the P-F emission with a plot of  $\ln(I/V) - V^{1/2}$  displays a linear relationship in the high-voltage region, as shown in Fig. 5 (d). The P-F emission results indicate that the carriers trapped in trap sites obtain enough energy, such as a high electric field or high temperature, that the trapped carriers are excited from the energy

barriers of the traps to the conduction band.<sup>28</sup> It is known that the transition of P–F emission, which is typically at high-voltage, is much higher because of the much closer spacing of the traps. Therefore, the electron occupation probability of the nearest traps is very low, since all the electrons are quickly swept out through P–F emission.<sup>41</sup> In our case, multiple RSs can be attributed to various conduction mechanisms, including the TAT model and P–F emission under a high electric field. Based on these analyses, we can understand the electron conduction mechanism in each RS. The conduction mechanism for LRS can also be explained by Ohmic conduction: In the low-voltage region, lots of traps in the  $\text{TiO}_x$  matrix and  $\text{SiO}_2$  NPs connect with each other, and this contributes to Ohmic conduction. Upon increasing the voltage, the conductive path into the  $\text{TiO}_x$  matrix and  $\text{SiO}_2$  NPs begins to be formed. When large current flows through the conductive path, the conduction mechanism in LRS is explained by Ohmic behavior with a slope of 1.13, as shown in Fig. 5 (b).

Figure 6 (a) – (e) show schematics of the energy band diagrams of the  $\text{TiO}_x$  and  $\text{TiO}_x@SiO_2$  NPs devices, respectively, in the initial and SET states. As shown in Fig. 6 (b), with the application of positive voltages to TE, the traps below the  $\text{TiO}_x$  conduction band are gradually filled with electrons. After all of the traps are filled (i.e., after exceeding the trap-filled limit voltage,  $V_{\text{TFL}}$ ), the current rapidly increases, and the  $\text{TiO}_x$  device switches from HRS to LRS. When negative voltage is applied to the TE, de-trapping of the oxygen vacancies occurs, and the  $\text{TiO}_x$  device transitions from LRS to HRS. The dominant mechanism in the  $\text{TiO}_x@SiO_2$  NPs device is almost the same as that in the  $\text{TiO}_x$  device. In the initial state of the  $\text{TiO}_x@SiO_2$  NPs device, the energy barrier exists at  $\text{TiO}_x/\text{SiO}_2$  NPs, as shown in Fig. 6 (c). Therefore, compared to the  $\text{TiO}_x$  device, more sufficient voltage is needed to pass across  $\text{TiO}_x$  and  $\text{SiO}_2$  NPs. Upon applying voltages to the  $\text{TiO}_x@SiO_2$  NPs device, the electrons can migrate from  $\text{TiO}_x$  to  $\text{SiO}_2$  NPs, and thus overcome the energy barrier of  $\text{TiO}_x/\text{SiO}_2$  NPs. The electrons move along the tilted conduction band of the  $\text{TiO}_x$  layer, and then the  $\text{TiO}_x$  device reaches LRS (LRS 1). When the higher voltage is applied to the  $\text{TiO}_x$  device, the trapped electrons could either hop to other trap sites or be excited to the conduction band. As a result, the current level abruptly increases, and the  $\text{TiO}_x$  device eventually reaches higher current levels (LRS 2 and LRS 3). When the negative voltage is applied to the electrode, the conductive filament ruptures, and the device switches from LRS to HRS.

## Conclusion

In conclusion, we have demonstrated an improvement in the optical and electrical characteristics of a  $\text{TiO}_x$  resistive switching device with the embedment of  $\text{SiO}_2$  NPs, which are structured with ITO/ $\text{TiO}_x@SiO_2$  NPs/ITO on glass substrate. The  $\text{TiO}_x@SiO_2$  NPs device structure shows a high transmittance over 95 % in the visible range. The embedment of  $\text{SiO}_2$  NPs into the  $\text{TiO}_x$  matrix induces higher oxygen vacancies in the  $\text{TiO}_x$  matrix; further, because Si–O has a higher bond dissociation energy than Ti–O, it determines the formation and rupture of the conductive path through the application of an electric field. The  $\text{TiO}_x@SiO_2$  NPs device exhibits stable bipolar resistive switching characteristics, and a distinguishable multi-level of four states (three of LRS and one of HRS) can be obtained by applying

voltage. Moreover, the device shows a long retention time for  $10^3$  s as well as good endurance for  $10^2$  cycles. The dominant switching mechanism is based on the conductive filament model, which includes the trap-controlled SCLC. After all the traps are filled out, the TAT and P–F emission gradually become dominant in the high-voltage region. The embedment of  $\text{SiO}_2$  NPs in the  $\text{TiO}_x$ -based device can lead to improved electrical characteristics, such as multi-level switching, as well as low-voltage operation with stable resistive states, thus making it a promising method for future non-volatile memory devices.

## Methods

### Synthesis and fabrication

$\text{TiO}_x$  was synthesized using the sol–gel method, which is based on the hydrolysis of alkoxides in alcoholic solutions in the presence of an acid catalyst. Titanium isopropoxide (TTIP,  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ , Aldrich Chemical Co., 97 %), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , Daejung 99.9 %), and nitric acid ( $\text{HNO}_3$ , Merck, 70 %) were used as the starting materials, and distilled (DI) water was used for hydrolysis. The molar ratio of the starting solution was 1 of TTIP, 1 of DI water, 25 of ethanol, and 0.2 of nitric acid.<sup>[42]</sup> The solution of nitric acid, DI water, and half ethanol was added dropwise to the solution of TTIP and ethanol at  $0^\circ\text{C}$  under continuous vigorous stirring. The transparent solution finally resulted, and it was diluted using ethanol with a ratio of 1:1.

### Fabrication of switching device

To fabricate the  $\text{TiO}_x$ -based switching memory device with a cross-bar array architecture, a glass substrate was first cleaned by wet cleaning through ultra-sonication for 10 min each in acetone, isopropyl alcohol, and DI water, before being dried in an oven at  $80^\circ\text{C}$  for 20 min. Next, the promoter was coated on the glass substrate at 1000 rpm for 10 s and 5000 rpm for 60 s to enhance the adhesion of the photoresist, after which negative photoresist (5214) was coated at the same condition, followed by soft baking at  $110^\circ\text{C}$  for 140 s. Then, the glass substrate was exposed to UV light for 3 s with photomask using an aligner. After being baked again at  $120^\circ\text{C}$  for 200 s, the glass substrate was exposed again to UV light for 7 s without photomask, after which it was soaked in developer for 60 s. Subsequently, ITO layer was deposited on the patterned photoresist using direct current sputtering, and the substrate was soaked in acetone for lift-off of the photoresist, leading to the BE patterns. In the next step, 50 nm-thick  $\text{TiO}_x$  film was coated on the patterned BE of ITO by the spin coating method at 5500 rpm for 60 s. For the one-step solution process, 230  $\mu\text{L}$  of  $\text{SiO}_2$  NPs (Nanocomposix,  $20 \pm 4$  nm) and 100  $\mu\text{L}$  of diluted  $\text{TiO}_x$  solution were mixed together under continuous stirring for 15 min, after which the mixed solution was coated with the same condition. Next, the coated  $\text{TiO}_x$  and  $\text{SiO}_2$  NPs-embedded  $\text{TiO}_x$  ( $\text{TiO}_x@ \text{SiO}_2$  NPs) were dried at  $80^\circ\text{C}$  for 20 min in an oven. All of the  $\text{TiO}_x$  and  $\text{TiO}_x@ \text{SiO}_2$  NPs films had an amorphous structure (Figure S4). Then, to obtain the TE pattern, the same process used for photoresist patterning and ITO deposition was performed repeatedly on the  $\text{TiO}_x$  and  $\text{TiO}_x@ \text{SiO}_2$  NPs layers. Finally, the cross-

bar array ReRAM structures with an active device area of  $100\ \mu\text{m}^2$  were obtained, as shown in Fig. 7 (a) and (b).

## Characterization

The structural characteristics were observed using atomic force microscopy (AFM, Bruker Corp. N8 NEOS) measurement. The scanning was performed using non-contact mode and a scan size of  $5.5\ \mu\text{m}^2$ . The cross-sectional specimens were prepared using a focused ion beam (FIB, FEI Helios 650) system, then examined using field effect transmission electron microscopy (TEM, JEOL Ltd. JEM-F200) with energy-dispersive spectroscopy (EDS). The optical transmittance was measured with ultraviolet-visible (UV-Vis, TEC5 MultiSpec) spectroscopy in the range from 400 to 800 nm. The thickness and optical constant of the  $\text{TiO}_x$  and  $\text{TiO}_x@SiO_2$  NPs layers were examined through spectroscopic ellipsometry (SE, J. A. Woollam-VASE) measurement from 1 to 5 eV with an incident angle of  $65^\circ$ . To accurately investigate the composition and chemical state of  $\text{TiO}_x$  and  $\text{TiO}_x@SiO_2$  NPs, x-ray photoelectron spectroscopy (XPS, ESCA Veresprobe II) was conducted using a monochromatic Al K $\alpha$  source ( $h\nu = 1486.7\ \text{eV}$ ) with a pass energy of 29.5 eV. The current–voltage (I–V) was measured using a semiconductor analyzer (Keithley-4200). During the I–V measurement, the bias was applied to the TE of ITO, and the BE of ITO was grounded under ambient conditions.

## Declarations

## Acknowledgements

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## Author contributions

S.Kwon and K. -B. Chung conceived the idea and designed the experiments. S. Kwon conducted the experiments and evaluated the data with help of M. -J. Kim. S. Kwon and K. -B. Chung wrote the manuscript. All authors read and approved the manuscript for submission.

## Competing interests

The authors declare no competing interests.

# Additional information

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## Figures

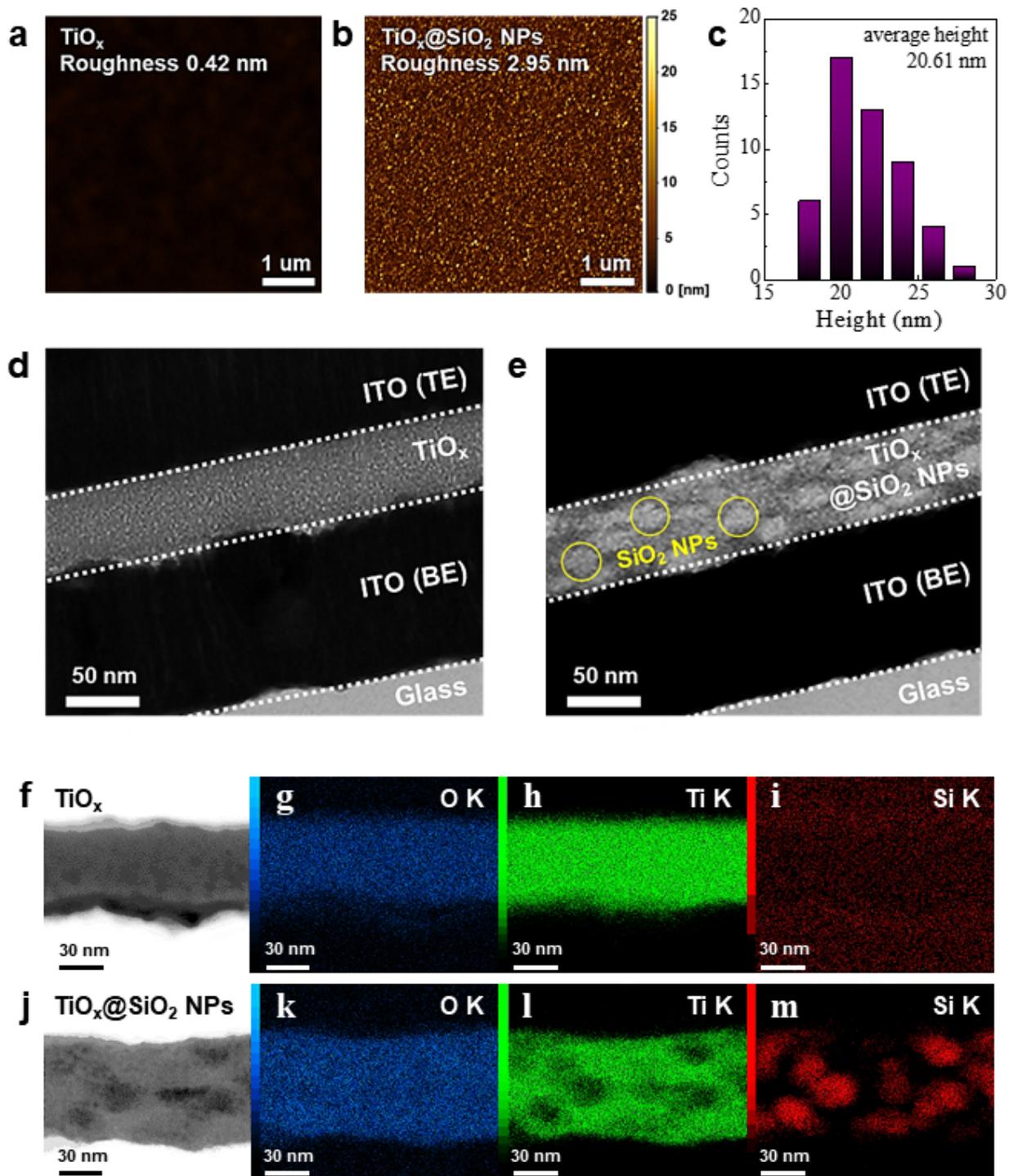
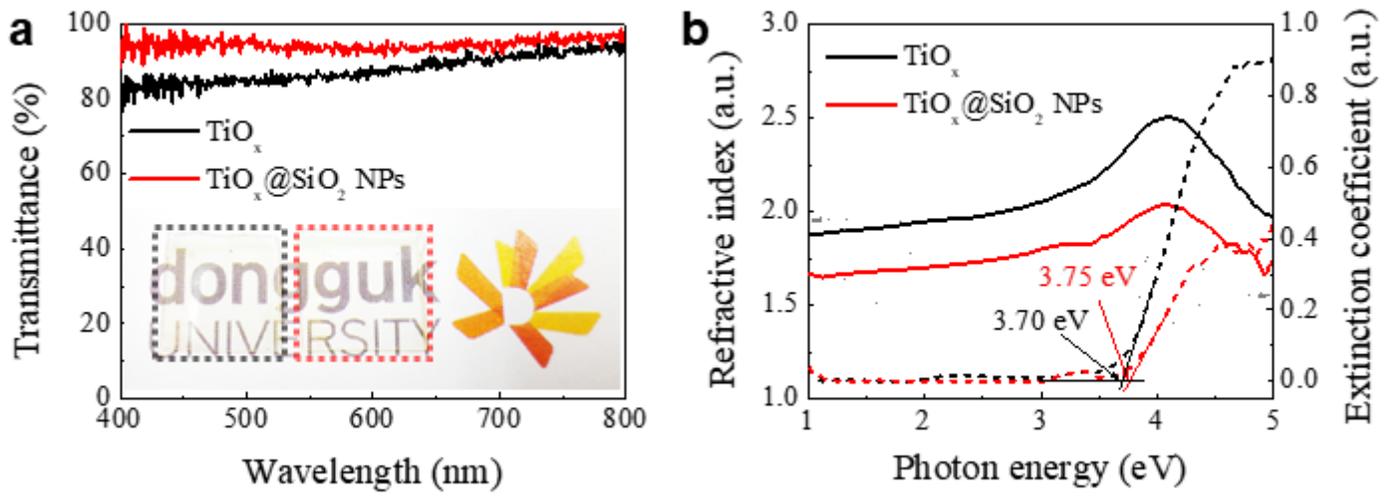


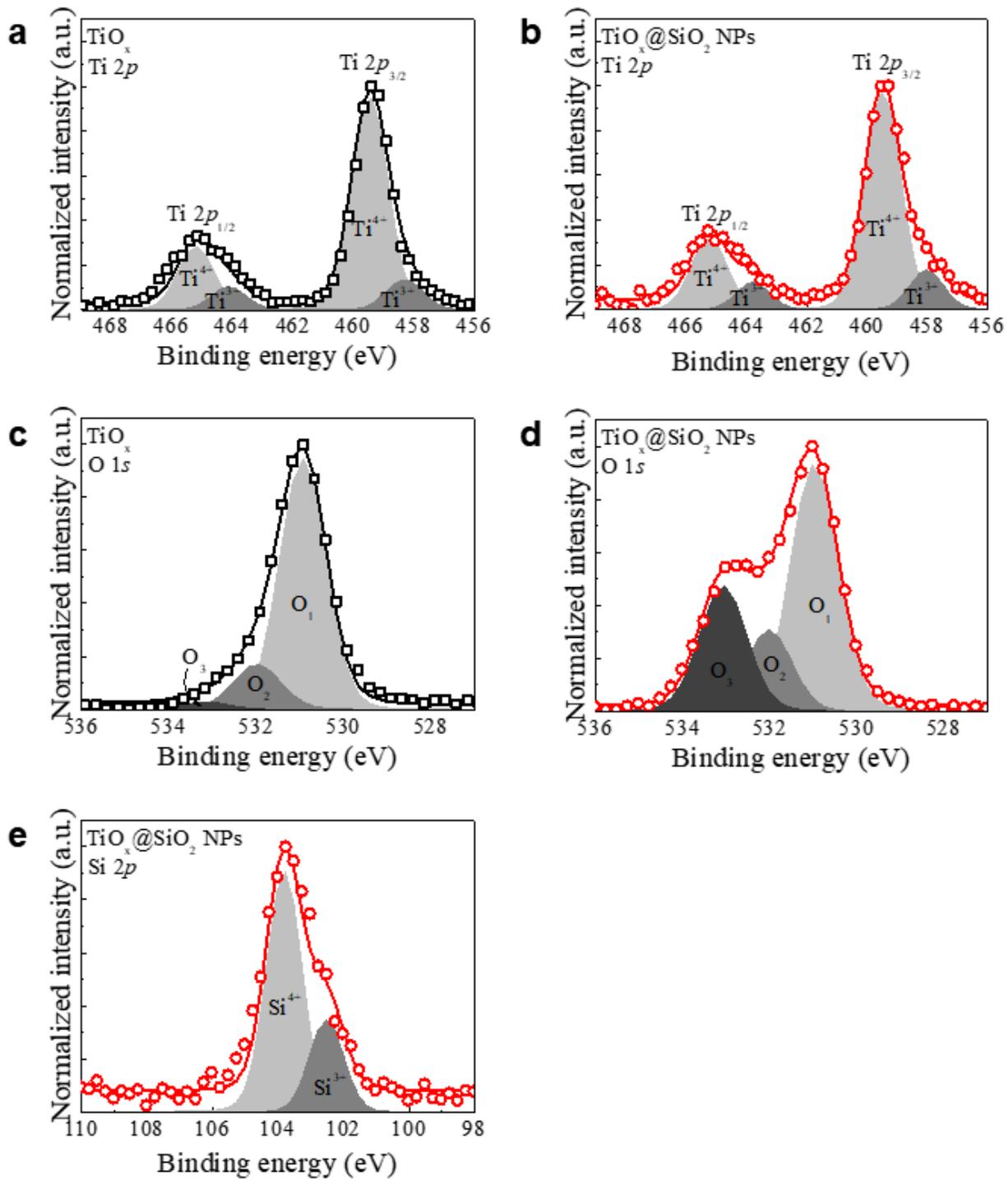
Figure 1

(a), (b) AFM topographic images, (c) average height of  $SiO_2$  NPs, (d), (e) cross-sectional TEM images, and (f) – (i) HAADF-STEM and EDS spectra of  $TiO_x$  and (j) – (m)  $TiO_x@SiO_2$  NPs structures.



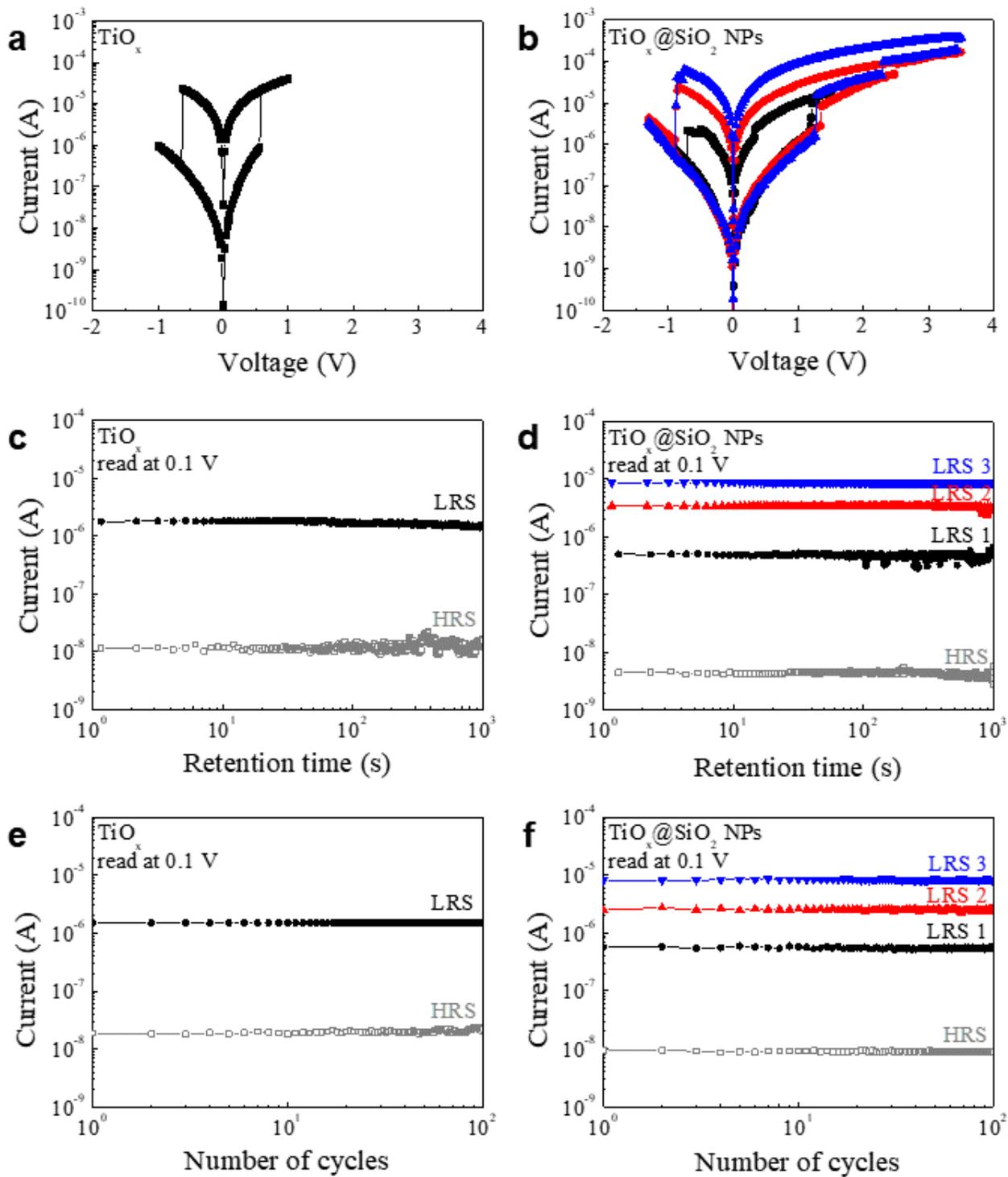
**Figure 2**

(a) Optical transmittance and (b) optical constants of the  $\text{TiO}_x$  and  $\text{TiO}_x@SiO_2$  NPs films. Inset shows the high transparency of the  $\text{TiO}_x$  (left) and  $\text{TiO}_x@SiO_2$  NPs (right) switching devices.



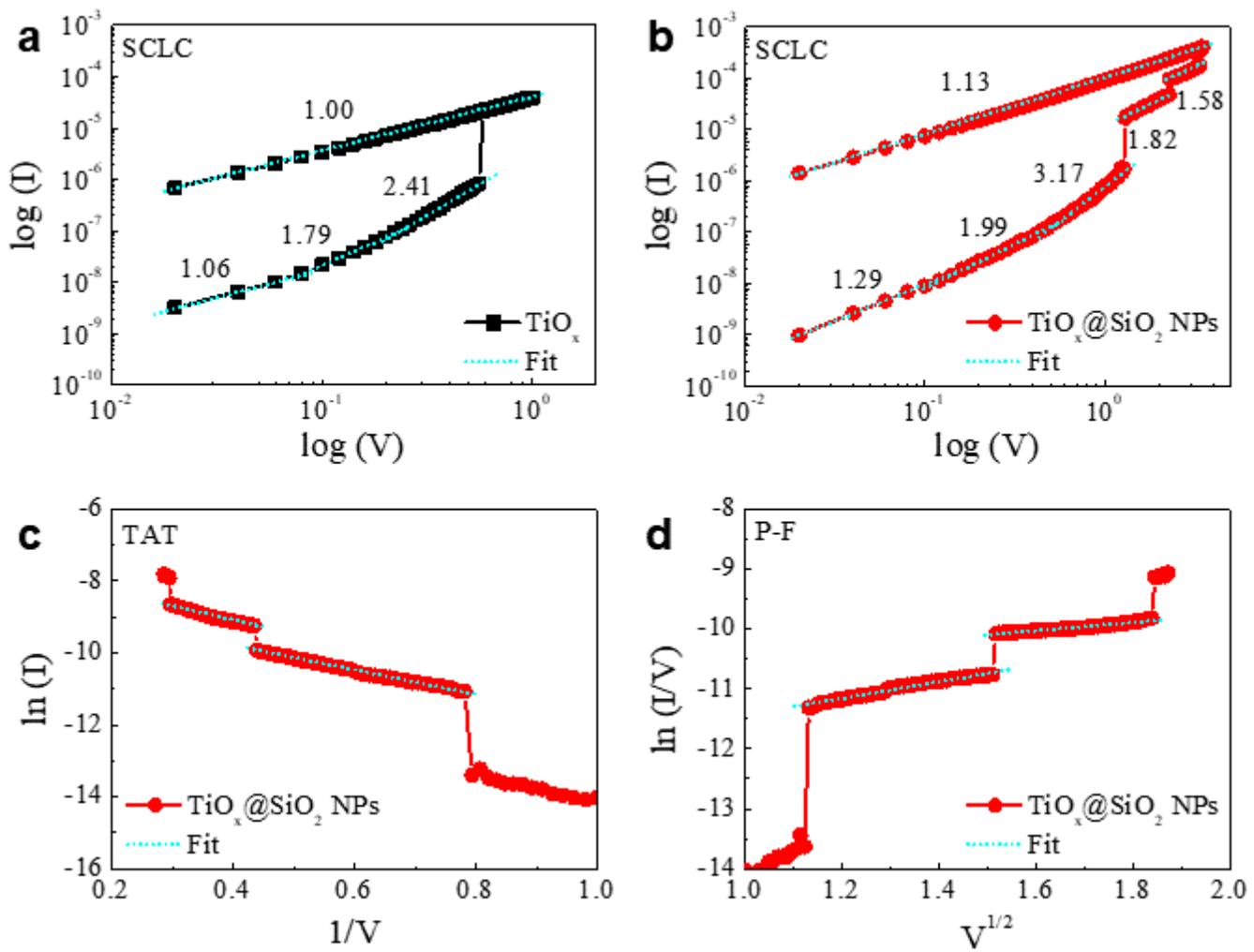
**Figure 3**

XPS core-level spectra of (a), (b) Ti 2p, (c), (d) O 1s for  $\text{TiO}_x$  and  $\text{TiO}_x @ \text{SiO}_2$  NPs films, and (e) Si 2p for  $\text{TiO}_x @ \text{SiO}_2$  NPs film.



**Figure 4**

(a), (b) Resistive switching curves, (c), (d) retention performance, and (e), (f) endurance performance of the TiO<sub>x</sub> and TiO<sub>x</sub>@SiO<sub>2</sub> NPs switching device.



**Figure 5**

Log I – log V plot of I-V curves of the (a) TiO<sub>x</sub> and (b) the TiO<sub>x</sub>@SiO<sub>2</sub> NPs switching devices. The TiO<sub>x</sub>@SiO<sub>2</sub> NPs implies (c) trap-assisted tunneling, and (d) Poole-Frenkel emission in the high-voltage region.

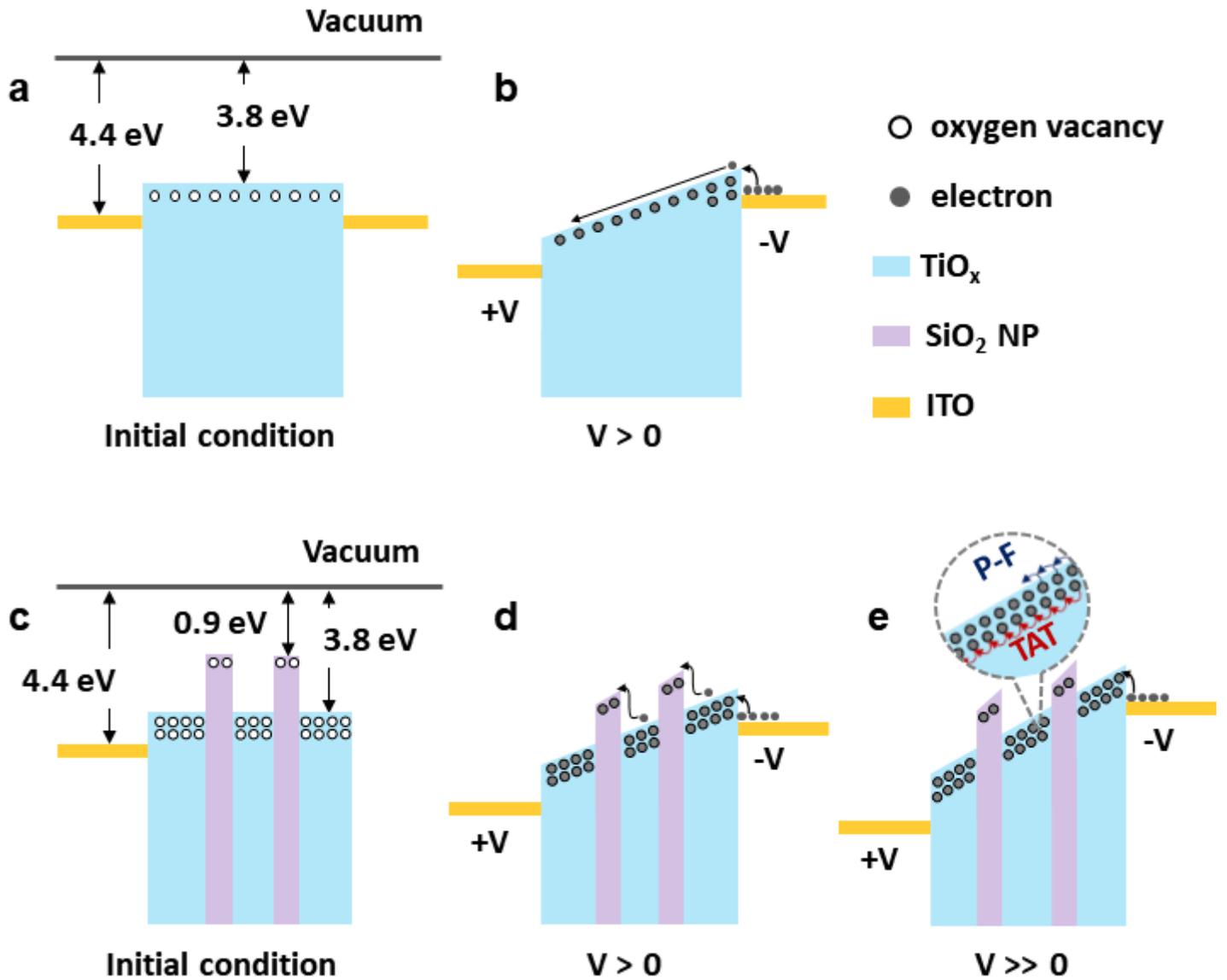
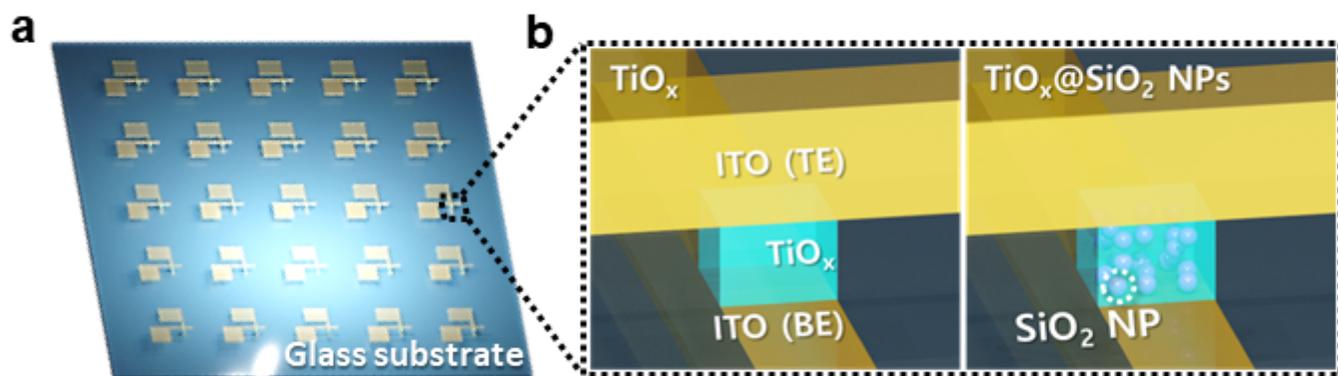


Figure 6

Schematic energy band diagrams for (a), (b) the TiO<sub>x</sub> device and (c) – (e) the TiO<sub>x</sub>@SiO<sub>2</sub> NPs under initial states and SET process.



**Figure 7**

(a) Schematic illustration of cross-bar arrays of the  $\text{TiO}_x$  switching device. (b) Enlarged view of the cross-section region of the switching device unit cell.

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