Prominent Thermodynamical Interaction with Surroundings on Nanoscale Memristive Switching of Metal Oxides

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ABSTRACT: This study demonstrates the effect of surroundings on a memristive switching at nanoscale by utilizing an open top planar-type device. NiOx and CoOx planar-type devices have exhibited a memristive behavior under atmospheric pressure, whereas TiO2-x planar-type devices did not show a memristive switching even under the same surroundings. A memristive behavior of TiO2-x planar-type devices has emerged when reducing an ambient pressure and/or employing a SiO2 passivation layer. These results reveal that a thermodynamical interaction with surroundings critically determines the occurrence of memristive switching via varying a stability of nonstoichiometry. Since this effect tends to be more significant for smaller devices with larger specific surface area, tailoring the surrounding effect by an appropriate passivation will be essential for high density devices.

KEYWORDS: Memristive switching, surrounding effect, planar device, redox, metal oxides

Memristive switching phenomena, which emerge in simple two terminal metal/oxide/metal sandwich structures, open up an interdisciplinary research field toward universal nonvolatile memory, artificial neural computing and so on.1−12 Since the resistance state programmed by an electric field must be maintained to obtain the nonvolatility of memory devices,13,14 the competition with thermal fluctuations from surroundings, which drives a state of switching material to a thermodynamically stable state, might be an inherent nature of memristive switching phenomena. In addition when decreasing the device size for high density memories, the surrounding effect must be amplified due to the large specific surface area. In this context, understanding the role of surroundings on the memristive switching phenomena is strongly required to design and control the features of nanoscale memristive switching. Although such knowledge as to the interactions with surroundings is still not comprehensive. The effects of oxygen on resistive switching have been examined mainly by varying the oxygen partial pressure during oxide thin film formations (i.e., different oxygen contents within films).15,16 However, none of previous works have demonstrated the direct experimental results as to the role of surrounding oxygen during switching. This is because in conventional capacitor-type device structures the resistive switching events are buried within the inside of switching layer, and it is relatively difficult to vary intentionally the surrounding oxygen near the conductive channel. Planar-type memristive devices offer an alternative approach to extract such information of memristive switching since the switching phenomenon in the planar-type devices is spatially opened and detectable. Our previous reports have demonstrated the feasibility of such planar-type devices to reveal some spatial features of memristive switching phenomena at nanoscale.17−20 However, the role of surroundings on the memristive switching phenomena has not been examined by using the planar-type devices in spite of the feasibility. Here we show the role of surroundings on nanoscale memristive phenomena by utilizing the planar-type devices comprised of TiO2-x, NiOx and CoOx. Comparing these different oxides on the memristive properties allow us to extract a surrounding effect due to their different thermodynamical stabilities. Results demonstrate that a thermodynamical interaction with surroundings critically determines the occurrence of memristive switching, highlighting the importance of tailoring such surrounding effect.

Figure 1 shows the device structures and the microscopic structures of TiO2-x based planar-type memristive devices.
Details of device fabrication are seen in Supporting Information. To construct the device structures, we utilized a pulsed laser deposition (PLD) and electron beam (EB) lithography. First, the line pattern with 100 nm width was fabricated onto a SiO2/Si(100) substrate by EB lithography. Polycrystalline TiO2x layer with 80 nm thickness was then deposited by PLD. The Pt nanoscale electrodes were patterned by EB lithography, followed by 100 nm Pt deposition by sputtering. We also fabricated the nanowire based planar-type devices for CoOx NiOx and TiO2x.20–23 The details of nanowire growth in situ formation method for nanowire heterostructures and the microstructures of CoOx and NiOx can be seen elsewhere.17–25 EB lithography was carried out to define the electrode pattern for these devices.26 We compare these planar-type devices (Pt/oxide/Pt) comprised of different oxides TiO2x, NiOx, and CoOx.

Figure 2 shows the typical current–voltage (I–V) curves of Pt/oxide/Pt planar-type devices, and the comparison between different oxides including TiO2x, NiOx, and CoOx. All experiments were performed under ambient condition at room temperature. The electrical polarity dependent bipolar memristive switching was observed in the planar-type devices comprised of CoOx and NiOx. In these devices, the SET process from high resistance state (OFF) to low resistance state (ON) occurs when applying positive electric field, whereas RESET process occurs at reversed negative electric field.17–20 Switching cycle endurance was confirmed at least up to 10^6 for both devices (see Supporting Information Figure S1). The retention data of the two devices were also shown in Figure 2, demonstrating the nonvolatility. On the other hand, the TiO2x planar-type device did not exhibit a memristive switching behavior even under the exact same surroundings. The resistance state was kept to be insulative even applying the electric field. Interestingly, current flows only when applying the positive voltage, whereas for the negative voltage, current does not flow and is kept to be below a current detection limit of 10 fA. The possible origin of this unique asymmetric I–V data will be discussed in terms of an electrochemical redox model in latter section. Similar trends were also found in the planar-type devices comprised of TiO2x nanowire (see Supporting Information Figure S2). Thus these results highlight the significant material dependence on the memristive switching behavior of planar-type devices under the same surrounding.

Here we question why only TiO2x planar-type devices did not exhibit clear memristive switching behavior under atmospheric condition at room temperature. First, there might be a size limitation to emerge TiO2 memristive switching because of the small size of the planar-type devices (100 nm). However, such size limitation scenario alone cannot explain above discrepancy because recent report has revealed the occurrence of TiO2x memristive switching at least down to several tens of nanometers scale.12–13 Second, a surrounding of materials might affect the memristive switching behavior because a nonstoichiometry of metal oxides, which in general determines an electrical conduction of metal oxides, is thermodynamically governed by an interaction with surroundings.17,28 Thus we altered the surroundings by varying the ambient pressure for the memristive switching measurements in the TiO2x planar-type devices.

Figure 3a shows the pressure dependence on the I–V data of TiO2x planar-type device. For the measurements, we reduced the ambient pressure from an atmospheric pressure down to 5 × 10⁻³ Pa and then increased it back to an atmospheric pressure.
pressure. We changed the ambient pressure by controlling the measurement chamber pressure. The oxygen partial pressure is assumed to be ca. 13.9% of each chamber pressure by taking into account the principle of turbo molecular pump.

Figure 3. Pressure dependences on TiO$\text{2}_{x}$ planar-type devices. (a) Series of $I$–$V$ data when varying the ambient pressure. Inset shows the five cycles of $I$–$V$ curves. (b) Series of retention data in various ambient pressures. (c) Cycle endurance of memristive switching measured at $\sim$5 Pa. Five volts was applied to read out the current. (d) ON/OFF current ratio as a function of ambient pressure. The data was collected after retention measurement of $10^5$ s. (e) ON and OFF state resistance values after SET and RESET processes in various ambient pressures. Readout voltage was 5 V. (f) Thermodynamical equilibrium lines for stoichiometric TiO$\text{2}$, NiO, and CoO.
Interestingly, the memristive switching behavior with the hysteresis loop tended to emerge as the pressure of surrounding atmosphere decreased down to 1 Pa. When further decreasing the pressure below 1 Pa, the hysteresis loop tended to be smaller, and the OFF state current significantly increased. The similar trend was also found even in the TiO$_2$-x planar-type nanowire devices, as shown in Supporting Information Figure S2. The $I$–$V$ measurements were performed at least for five cycles to ensure the reproducibility, as shown in the insets of Figure 3a. Figure 3b shows the retention data when varying an ambient pressure. The retention data well corresponds to the trend of hysteresis in $I$–$V$ data, and the larger hysteresis loop the larger difference between ON and OFF currents for all retention measurements. Switching cycle endurance in reduced ambient pressure conditions was also confirmed at least up to $10^9$, as shown in Figure 3c. Thus these data consistently demonstrate the emergence of memristive switching behavior in the TiO$_2$-x planar-type device when reducing atmosphere pressure. To extract more quantitatively the pressure dependence, Figure 3d,e shows the variations in the ON/OFF resistance ratio and the resistance values of both ON and OFF states when varying an ambient pressure. The ON state resistance is defined as a resistance value read at 5 V after retention measurement of $10^3$ s. SET process with the compliance current of $10^{-7}$ A was performed before the retention measurement. The OFF state resistance is defined as a resistance value read at 5 V after retention measurement of $10^3$ s. RESET process with the applied voltage of $-10$ V was performed before the retention measurement. The ON/OFF ratio showed the maximum at around 5 Pa, and the resistance values of both ON and OFF states increased with increasing the ambient pressure, especially around 1–100 Pa range. Since it is well-known that oxygen vacancies can act as a donor for n-type metal oxides in terms of the concentration variation of oxygen vacancies (i.e., mobile carrier concentrations). These results indicate that TiO$_2$-x based planar-type memristive devices require a non-stoichiometric TiO$_{2-x}$, whose degree of nonstoichiometry is somewhere in the middle range between stoichiometric insulative TiO$_2$ and highly conductive TiO$_{2-x}$ with plenty of oxygen vacancies. Considering a thermodynamical stability of metal oxides in terms of the Gibbs’ formation free energy (as shown in Figure 3f)$^{31}$, the thermodynamical equilibrium line for stoichiometric TiO$_2$ is located at oxygen partial pressure range much lower than atmospheric oxygen partial pressure (about 2 × $10^4$ Pa). Thus the interaction with surroundings of atmospheric condition strongly drives the composition of TiO$_{2-x}$ to a stoichiometric insulative TiO$_2$. On the other hand, the thermodynamical equilibrium lines for CoO and NiO are located at oxygen partial pressure ranges much higher than that of TiO$_2$. This indicates that for CoO$_x$ and NiO$_x$, the thermodynamical driving force to be a stoichiometric insulator that is much weaker than TiO$_{2-x}$ under atmospheric oxygen partial pressure. Although these explanations based on the thermodynamical equilibrium cannot capture quantitatively the details of dynamic reactions of nonstoichiometric oxide surfaces and/or grain boundaries,$^{32}$ the substantial discrepancy between TiO$_2$ and others (NiO and CoO) on the thermodynamic stability at atmospheric pressure should be qualitatively significant. This seems be consistent with the discrepancy between TiO$_{2-x}$, NiO$_x$, and CoO$_x$ on the memristive behaviors of planar-type nanowire devices, since the TiO$_{2-x}$ planar-type devices under atmospheric conditions was kept to be an insulator even while applying an electric field. According to a model for memristive switching of n-type oxides-TiO$_{2-x}$, the nonstoichiometry induced by an electric field should be somehow stable to maintain the nonvolatile memory effects. Results in Figure 3 infer that for only certain surrounding conditions, the electric field-induced nonstoichiometry might be maintained. In other words, having or creating such surrounding conditions is essential to realize the memristive switching. Thus, the thermodynamical stability of non-stoichiometry, which is determined by interacting with the surroundings, can well explain why only TiO$_{2-x}$ planar-type devices did not exhibit clear memristive switching behaviors under atmospheric condition.

Within the framework of an electrochemical redox model for n-type TiO$_2$, SET process is related to reduction and RESET process is related to oxidation.$^{29–31}$ In the experiments of Figure 3a, SET process occurs at positive voltage, and RESET occurs at negative voltage. Based on these correspondences, the trends of Figure 3a can be interpreted as follows. When an ambient pressure is relatively high ($10^2$–$10^3$ Pa), current flows only when applying the positive voltage, whereas the current level was kept to be below 10 fA for the negative voltage sweep. On the basis of above model, the asymmetry of $I$–$V$ data can be understood in terms of the competition between an electric field induced SET (or RESET) process and a thermodynamical interaction process with surroundings. For relatively high pressure range, the interaction with surroundings strongly drives TiO$_{2-x}$ to be more insulative. When applying positive voltage, SET process drives TiO$_{2-x}$ to be more conductive via reduction, while the thermodynamical surrounding effect tends to oxidize TiO$_{2-x}$. During SET process, as the applied voltage increases, current starts to flow due to the change of resistances when the surrounding oxidation effect cannot compensate the effect of SET process.$^{33}$ However, the strong oxidation effects from the surrounding do not allow the conductive TiO$_{2-x}$ to remain due to a prompt oxidization when decreasing voltage. On the other hand, for negative voltage sweep, both RESET process and the surrounding effect tend to oxidize TiO$_{2-x}$. This results in highly insulative TiO$_{2-x}$ and therefore the current is kept to be below the current detection limit for negative voltage sweep. Thus an electrochemical redox model well explains the asymmetric $I$–$V$ trends of Figure 3a for a relatively high pressure range.

When a pressure decreases, both ON and OFF currents tend to increase, and the shape of $I$–$V$ data tends to be symmetric from the asymmetric shape in Figure 3a. These trends can be also interpreted in terms of above model. Decreasing an ambient pressure weakens an oxidization effect from surroundings. As such, a conductive TiO$_{2-x}$ induced by electric field (SET process) can be more maintainable even when interacting with surroundings. As a result, the hysteresis loop tends to be larger during SET process as the pressure decreases down to 1–5 Pa. When further decreasing a pressure below 1 Pa, a reduction effect from the surroundings tends to be stronger. Since this effect competes with RESET (oxidization) process, creating insulative OFF state tends to be difficult, and in both SET and RESET processes the electrical conduction is kept to be conductive, as seen in Figure 3a. The detail analysis of the trend is provided in Supporting Information Figure S7. Thus the higher stability of conductive TiO$_{2-x}$ results in the symmetric shape of $I$–$V$ for relatively low pressure range. These interpretations based on the electrochemical redox
model highlight the essential role of surroundings on the emergence of memristive switching behavior.

Although above implications were obtained from the results of planar-type devices, the principle might be applicable even for capacitor-type devices. In a capacitor-type device, a memristive switching occurs underneath electrodes, and the electric field induced electrical conduction must exist within a solid material\textsuperscript{12,29,31,33}. Therefore the stability of nonstoichiometry for capacitor-type devices must rely on the interaction with surrounding solid matrix rather than atmosphere. As shown in Supporting Information Figure S3, we have observed the occurrence of memristive switching in TiO\textsubscript{2-x} capacitor-type device even under atmospheric condition, as reported in elsewhere\textsuperscript{29–31}. Comparison between Figure 2 and Supporting Information Figure S3 indicates that oxygen vacancies within TiO\textsubscript{2-x} solid matrix are thermodynamically rather stable more than that at the oxide surface. This essentially allows the occurrence of memristive switching for capacitor-type devices even in an atmospheric condition. To demonstrate directly the difference on the interaction with surrounding atmosphere, we examine the effects of different surrounding gases on the ON state current of both devices (see Supporting Information Figure S4.). In the planar-type devices, introducing oxidation atmosphere such as ozone-contained gas resulted in the decrease of ON state current, which is consistent with the general trend of n-type oxides\textsuperscript{27,28}. This trend for n-type TiO\textsubscript{2-x} is completely opposite to that for p-type NiO\textsubscript{x} and CoO\textsubscript{x}\textsuperscript{18,19} where introducing oxidation atmosphere resulted in the increase of ON state current. On the other hand, the capacitor-type devices were clearly insensitive to the variation of different surroundings. Thus the interaction with the surroundings significantly differs from between the two. Note that the surrounding effect might not be negligible even for capacitor-type devices when reducing the device size with large specific surface area. However there is a discrepancy between our results and a previous report where the memristive switching was observed in several tens of nanometers scale even under atmospheric conditions\textsuperscript{12}. The difference can be interpreted in terms of the difference of specific surface area for both device geometries. Since the surrounding effect must be amplified when the electrical conduction area exposed to atmosphere increases, a specific surface area determines the degree of surrounding effects. In the case of reported cross-bar Pt/TiO\textsubscript{2}/Pt nanodevices\textsuperscript{18}, the device is constructed by monolithic TiO\textsubscript{2} thin films sandwiched by nanopatterned electrode. In this case, the electrical conduction area underneath the electrode is mainly surrounded by TiO\textsubscript{2} solid matrix and Pt electrode. Therefore the specific surface area exposed to atmosphere is rather limited in this device geometry. On the other hand, our planar-type device is totally exposed to atmosphere, and the specific surface area is much larger than the above conventional sandwich device geometry. However, our findings are quite useful when a via-hole type device, which is generally used in CMOS process to isolate electrically a device from an adjacent one, is employed.

Above our findings as to the role of surroundings on the memristive switching behaviors highlight the importance of tailoring a surrounding condition for small memristive devices. Use of a solid passivation layer might be one of the promising solutions for such purpose. Thus we examine the effect of solid passivation layer on the TiO\textsubscript{2-x} planar-type devices. Figure 4a,b shows the schematic image and FESEM image of the passivated TiO\textsubscript{2-x} planar-type device. SiO\textsubscript{2} amorphous layer with the thickness of 300 nm was utilized as the passivation layer, which was deposited onto the planar-type devices at room temperature by sputtering. Figure 4c shows the $I$–$V$ curve of passivated TiO\textsubscript{2-x} planar-type device measured under atmospheric condition. Note that we have confirmed the absence of any electrical conduction when depositing only SiO\textsubscript{2} passivation layer between electrodes. Contrary to nonpassivated TiO\textsubscript{2-x} planar-type device, the passivated planar-type TiO\textsubscript{2-x} device exhibited the clear memristive switching with large hysteresis loop even under atmospheric condition. The endurance data of memristive switching in passivated TiO\textsubscript{2-x} planar-type device is shown in Figure 4d. This clearly shows that the presence of SiO\textsubscript{2} passivation strongly enhances the memristive switching. This is presumably due to higher stability of an oxygen vacancy state at a solid interface and/or a lower diffusion constant of oxygen ion within a solid when compared with the diffusion constant of oxygen molecules in a vapor. Although investigations need to be undertaken to reveal further a defect stability within an oxide, these results are quite encouraging to tailor a memristive switching at small scale.

In conclusion, we demonstrate the role of surroundings on the memristive switching behavior by utilizing a planar-type device. NiO\textsubscript{x} and CoO\textsubscript{x} planar-type devices have exhibited the memristive behavior under atmospheric condition, whereas TiO\textsubscript{2-x} planar-type devices did not show clear memristive switching even under the same surroundings. The memristive behavior of TiO\textsubscript{2-x} planar-devices has emerged when reducing ambient pressure and/or employing a SiO\textsubscript{2} passivation layer. These material dependences of memristive behaviors in open top planar-type devices reveal that a thermodynamically stable state governed by the interactions with surroundings critically determines the occurrence of memristive switching, indicating the importance of tailoring the surrounding effects with appropriate passivation layers, especially for small devices.

\begin{figure}[h]
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\includegraphics[width=0.8\textwidth]{figure4.png}
\caption{Effect of passivation on nanoscale TiO\textsubscript{2-x} memristive switching. (a) Schematic illustration and (b) FESEM image of SiO\textsubscript{2} passivated TiO\textsubscript{2-x} planar-type device. SiO\textsubscript{2} passivation layer of 300 nm was formed on TiO\textsubscript{2-x} planar-type device. (c) $I$–$V$ curve and (d) switching endurance of passivated TiO\textsubscript{2-x} planar-type device measured in atmospheric condition at room temperature, respectively.}
\end{figure}

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Switching endurance data of the devices comprised of MgO/ NiOx nanowire and MgO/Co3O4 nanowire (Figure S1), additional structural characterization and electrical transport properties of planar-type MgO/TiO2 nanowire devices (Figure S2), planar-type TiO2 nanodevice (Figure S6), capacitor-type TiO2-oxiodevice (Figure S3) including I-V curves, retention data and analysis (Figure S4, S5, S7), and details of experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

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**REFERENCES**

