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**In situ** control of oxygen vacancies in TiO$_2$ by atomic layer deposition for resistive switching devices

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Abstract

Oxygen vacancies ($V_O$) have profound effects on the physical and chemical performance of devices based on oxide materials. This is particularly true in the case of oxide-based resistive random access memories, in which memory switching operation under an external electrical stimulus is closely associated with the migration and ordering of the oxygen vacancies in the oxide material. In this paper, we report on a reliable approach to \textit{in situ} control of the oxygen vacancies in TiO$_2$ films. Our strategy for tight control of the oxygen vacancy is based on the utilization of plasma-enhanced atomic layer deposition of titanium oxide under precisely regulated decomposition of the precursor molecules (titanium (IV) tetraisopropoxide, Ti[OCH(CH$_3$)$_2$]$_4$) by plasma-activated reactant mixture ($N_2 + O_2$). From the various spectroscopic and microstructural analyses by using Rutherford backscattering spectrometry, x-ray photoelectron spectroscopy, high-resolution transmission electron microscopy, confocal Raman spectroscopy, and spectroscopic ellipsometry, we found that the precursor decomposition power ($R_F$) of plasma-activated reactant mixture determines not only the oxygen vacancy concentration but also the crystallinity of the resulting TiO$_x$ film: nanocrystalline anatase TiO$_x$ with fewer oxygen vacancies under high $R_F$, while amorphous TiO$_x$ with more oxygen vacancies under low $R_F$. Enabled by our controlling capability over the oxygen vacancy concentration, we were able to thoroughly elucidate the effect of oxygen vacancies on the resistive switching behavior of TiO$_x$-based memory capacitors (Pt/TiO$_x$/Pt). The electrical conduction behavior at the high resistance state could be explained within the framework of the trap-controlled space-charge-limited conduction with two characteristic transition voltages. One is the voltage ($V_{SCL}$) for the transition from Ohmic conduction to space-charge-limited conduction, and the other is the voltage ($V_{TFL}$) for transition from space-charge-limited conduction to trap-filled-limited conduction. In this work, we have disclosed for the first time the dependence of these two characteristic transition voltages (i.e., $V_{SCL}$ and $V_{TFL}$) on the oxygen vacancy concentration.

[S] Online supplementary data available from stacks.iop.org/Nano/24/295202/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Resistive random access memory (ReRAM) is a non-volatile memory, in which switching is operated by the resistance change under an external stimulus such as voltage or current [1–4]. Recently, ReRAM has drawn enormous attention as a prospective next-generation memory due to its notable memory performance such as fast switching
(<10 ns), low power consumption (∼1 pJ/operation), multi-level switching, excellent cyclability (>10^12), and long retention period (>10 years) [5–10]. Together with these promising characteristics, a very simple memory cell structure of a capacitor-like metal/oxide/metal stacking configuration is advantageous for realizing ReRAM devices with ultra-high storage density via highly scalable cross-point and/or multi-level packaging [5–7].

Resistive switching (RS) behavior has been commonly observed in various materials including transition metal oxides, metal halides, perovskites, and chalcogenides [2, 4, 11]. Among them, titanium oxide (TiO_x) is one of the most extensively studied switching materials owing to its simple preparation process and compatibility with conventional Si-based semiconductor device processes [5, 7, 9, 12, 13]. The formation and rupture of the local conducting filaments (CFs) have been considered as the mechanism governing the RS phenomena in various switching materials [14–17]. In particular, in the case of TiO_2-based ReRAM devices, the CFs have been proven to be the oxygen deficient Magnéli phase (Ti_{x}O_{2x−1}) that is formed by the field-induced drift of the oxygen vacancies (V_O) during the switching operation [12, 13, 15]. In general, TiO_x exhibits n-type semiconducting behavior due to the presence of the oxygen vacancy (V_O) [18–20]. In these respects, delicate control of the oxygen vacancy (V_O) is very important for guaranteeing reliable memory switching operations of TiO_2-based ReRAM devices. It has been widely accepted that variation in the stoichiometry of TiO_x leads to alteration of the oxygen vacancy (V_O) concentration [18–23]. Accordingly, establishment of a method for reliable control over the stoichiometry may allow one to systematically investigate the effect of the oxygen vacancy (V_O) on the RS behavior of titania-based ReRAM devices.

Previously, oxygen deficient TiO_x (i.e., x < 2.0) has been prepared by magnetron sputtering, pulsed laser deposition, and chemical vapor deposition (CVD) under controlled oxygen partial pressure, sol–gel processes, electron- or ion-beam bombardment, or thermal annealing of TiO_2 under reducing ambient [18, 24–28]. However, most of these approaches have some difficulties either in systematic control of the stoichiometry (i.e., the amount of oxygen vacancies) of TiO_x or in uniform deposition of the material over a technologically relevant large scale [18, 27, 29]. In an attempt to resolve these issues, the atomic layer deposition (ALD) technique has recently been employed for the growth of stoichiometry-controlled TiO_x films. ALD offers many distinct merits over conventional physical (PVD) or chemical vapor deposition (CVD) techniques in terms of precise control of the composition and thickness at atomic length scale by virtue of its self-limiting growth characteristics [30–32]. In fact, recent studies have shown that modification of the stoichiometry and electrical resistance of titania films can be achieved by appropriately altering ALD process conditions [33, 34].

In this paper, we report on in situ control of the stoichiometry of TiO_x material by ALD and also on the effect of the oxygen vacancy (V_O) on the RS behavior of TiO_x-based ReRAM capacitors. We employed a plasma-enhanced atomic layer deposition (PEALD) technique using titanium (IV) tetraisopropoxide (Ti(OCH(CH_3)_2)_4, TTIP) as a precursor, since it, compared to its thermal counterpart (i.e., thermal ALD), offers a large degree of freedom in the choice of processing conditions and thus in the deliberate engineering of the film properties [31]. Systematic control of the stoichiometry of TiO_x films could readily be achieved by adjusting the reactions between the precursor (i.e., TTIP) and the plasma-activated reactant gas molecules (i.e., O_2 + N_2 mixture). Enabled by our in situ control over the stoichiometry, the effect of oxygen vacancy (V_O) not only on the RS behavior of TiO_x-based ReRAM capacitors, but also on the conduction mechanism at the high resistance state (HRS), could successfully be disclosed. We investigated the interplay between the PEALD processing conditions, the amount of oxygen vacancies (V_O), and the electrical properties of TiO_x thin films by using a variety of characterization techniques including Rutherford backscattering spectrometry (RBS), transmission electron microscopy (TEM), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), confocal Raman spectroscopy, spectroscopic ellipsometry (SE), and current–voltage (I–V) characteristics measurements.

2. Experimental details

2.1. Substrate preparations

We employed two different kinds of substrates for PEALD of titanium oxide films: Si(001) and Pt-coated Si(001). The Si(001) substrates used in this study were thoroughly cleaned by using a copious amount of acetone, isopropyl alcohol, and deionized water. They were dried with a strong stream of nitrogen prior to use. On the other hand, Pt-coated Si substrates were prepared by sequentially depositing TiO_2 and Pt on a Si(001) wafer. A 7 nm-thick PEALD-grown TiO_2 layer was employed in order to improve the adhesion between the Pt layer and the Si(001) substrate. The Pt layer was deposited by electron-beam evaporation at room temperature using a high purity Pt slug (99.99%).

2.2. Plasma-enhanced atomic layer deposition (PEALD) of TiO_x

TiO_x films were deposited either on Si(001) substrates or Pt-coated Si(001) substrates by PEALD at a substrate temperature of 150°C by using a showerhead-type ALD system (CN1, Korea). A unit PEALD cycle was composed of the following four consecutive steps: (1) precursor exposure, (2) N_2 purging, (3) plasma exposure, and (4) another N_2 purge. Titanium (IV) tetraisopropoxide (Ti(OCH(CH_3)_2)_4, TTIP, 99.99%) was used as a precursor. The stainless steel canister containing TTIP was heated to 40°C to gain sufficient vapor pressure. The generated TTIP vapor was delivered to the reaction chamber at a flow rate of 100 sccm by using nitrogen as a carrier gas. The gas feeding line between the canister and the reaction chamber was heated to 60°C to prevent precursor condensation in the feeding line during the
precursor (i.e., TTIP), high purity nitrogen gas was introduced to the reaction chamber at a flow rate of 200 sccm for 10 s in order to remove the unreacted TTIP molecules and also the by-products (e.g., H₂O, CO₂, CO, etc.). High purity O₂ or a mixture of O₂ and N₂ at a total flow rate of 100 sccm was used as a reactant at a constant radio frequency (13.56 MHz) plasma power of 200 W. The ratio (R₂) of the O₂ flow rate to the total flow rate of mixture gas (i.e., F₀₂ + Fₙ₂ = 100 sccm, where F₀₂ and Fₙ₂ are the flow rates of oxygen and nitrogen gas, respectively) was systematically varied to be R₂ = 1.00, 0.75, 0.50 or 0.25. The substrate exposure durations to the precursor and the reactant plasma were 2 and 3 s, respectively. After the plasma exposure step, purging of the reaction chamber by nitrogen gas was carried out for 10 s to remove the by-products from the reaction chamber.

2.3. **Rutherford backscattering spectrometry (RBS)**

The contents of titanium and oxygen in the PEALD TiOₓ films were determined by RBS, using 2 MeV ⁴He²⁺ ions, with the ion beam at normal incidence to the specimen surface and with a backscattering angle of 170°. Data were evaluated by using the Rump program [35]. In the RBS spectra, the signals from Ti, O, Pt and Si were overlapped, and the composition was determined from the front edges of each element. The analyses of the stoichiometric ratios by RBS have absolute accuracies better than 1%, which is applicable for stoichiometric comparisons of titanium and oxygen contents between specimens [36].

2.4. **Microstructure analyses: transmission electron microscopy (TEM) and x-ray diffraction (XRD)**

Microstructural analyses on the PEALD TiOₓ films were carried out by cross-sectional TEM (Technai F30, FEI, USA), operated at a primary beam energy of 300 kV. Further analyses on the crystalline structure of the TiOₓ films were made by XRD (RU 200B, Rigaku, Japan) using Cu Kα radiation (λ = 1.5418 Å) operating in θ–2θ configuration at 15 kV and 20 mA. The scan speed and increment were 4° min⁻¹ and 0.02°, respectively.

2.5. **Confocal Raman spectroscopy**

A confocal Raman microscope was utilized to characterize the structural properties, i.e., the crystalline degree of the PEALD TiOₓ films. The 632.8 nm line of a He–Ne laser (05-LHP-847, Melles Griot) beam was delivered to the microscope (BX51, Olympus) through a single-mode optical fiber (5 μm core diameter, P1-630A-FC-10, ThorLabs). The laser beam was filtered by a narrow band interference filter (MaxLine Laser-Line Filter, LL01-633, Semrock), and then directed into the high numerical aperture objective (MPlan 50×, Olympus). The Rayleigh scattering was removed using a Raman filter (RazorEdge Raman Filter, LP02-633RE-25, Semrock) and Raman scattering from a TiO₂ film was guided through a pinhole (50 μm diameter) into a spectrograph equipped with a TE-cooled CCD. The excitation laser power was adjusted to 8 mW and Raman spectra were obtained at multiple spots on the sample for 10 s.

2.6. **X-ray photoelectron spectroscopy (XPS)**

The binding natures of the PEALD TiOₓ films were analyzed by XPS with 1253.6 eV radiation from a Mg anode. It has been reported that the binding peaks of the Ti 2p XPS spectrum can be altered by Ar ion bombardment [37]. Thus, the XPS analyses were carried out using as-prepared samples grown on Si substrates. The resulting XPS spectra were calibrated in binding energy by referencing to the C 1s peak from contamination at 284.6 eV. The XPS spectra for the O 1s level were fitted using elemental bands of Gaussian/Lorentzian shape after background subtraction of the spectra with a Shirley-type curve.

2.7. **Spectroscopic ellipsometry (SE)**

The optical properties including refractive index (n) and absorption were obtained from analyses of the ellipsometry spectra of the amplitude ratio (ψ) and phase difference (Δ) measured by SE (M2000D, J A Woollam). The ψ and Δ spectra were measured at three incidence angles of 65°, 70°, and 75° within the wavelength (λ) of 190–1000 nm. Information on the refractive index (n) and extinction coefficient (k) was obtained as a result of inversion of the SE spectra and film thicknesses of each layer which were obtained from the Tauc–Lorentz (TL) model combined with the effective-medium approximation (EMA) [38]. The resulting refractive index (n) and extinction coefficient (k) were used to determine the absorption coefficient (α) and the coordination number (Nₑ). The analytical method and procedure for α and Nₑ will be discussed in more detail later.

2.8. **Fabrication of the Pt/TiOₓ/Pt capacitors and RS characterization**

Extended arrays of Pt/TiOₓ/Pt microcapacitors were fabricated to investigate the RS behavior. 45 nm-thick TiOₓ films were grown on Pt-coated Si(001) substrates. Subsequently, circular 100 nm-thick Pt top electrodes with a diameter of 100 μm were fabricated by e-beam evaporation of Pt through a metal shadow mask at room temperature. The RS behavior of the resulting capacitor arrays was investigated by performing current–voltage (I–V) measurements at room temperature using a semiconductor characterization system (Keithley, SCS-4200). A voltage bias was applied to the top electrode, while the bottom electrode was grounded. The voltage scan was started from 0 V and increased by 0.01 V at each sweep. The current compliance was set at 10 mA to prevent the capacitors from permanent electrical breakdown during the voltage sweeps for both the electroforming and the SET from HRS to low resistance state (LRS).
can be attributed to the reduced precursor decomposition power of the plasma-activated reactant gas molecules, compared to that at \( R_F = 1.00 \).

RBS analyses were performed to determine the exact chemical composition of our TiO\(_x\) films. Table 1 presents the effect of the PEALD process conditions on the chemical composition of the resulting TiO\(_x\) films. According to our RBS analysis, the value of \( x \) in PEALD TiO\(_x\) films increases from 1.62 to 1.70, as \( R_F \) varies from 0.25 to 1.00 (see supplementary data figure S1 available at stacks.iop.org/Nano/24/295202/mmedia). This result indicates that one may readily control the oxygen vacancy (V\(_O\)) concentration in TiO\(_x\) film by deliberately adjusting the precursor decomposition power (namely, \( R_F \)) of the plasma-activated reactant gas molecules [31].

3.2. Microstructural analyses on PEALD TiO\(_x\) films

Figure 1 shows cross-sectional TEM micrographs of TiO\(_{1.62}\) and TiO\(_{1.70}\) films grown on Pt-coated Si(100) substrates by PEALD. It is evident from the micrographs that oxide films grown under the present PEALD process conditions are highly uniform. From close examination of the respective magnified TEM micrographs in figures 1(b) and (d), we found that the precursor decomposition power (\( R_F \)) of the plasma-activated reactant gas molecules can influence the formation of oxide nanocrystallites. The TiO\(_{1.62}\) film formed at \( R_F = 0.25 \) turned out to be completely amorphous (figure 1(b)). On the other hand, the microstructure of the TiO\(_{1.70}\) film formed at \( R_F = 1.00 \) was characterized by a random distribution of nanometer-sized crystallites in the amorphous oxide matrix (figure 1(d)).

In an attempt to reveal the crystallographic phase of the nanocrystallites in our oxide films, we performed XRD analysis. No diffraction peaks for the TiO\(_2\) crystalline phase were observed in the XRD spectra for any of our PEALD TiO\(_x\) films (supplementary data figure S2 available at stacks.iop.org/Nano/24/295202/mmedia). This would arise from the low deposition temperature (150°C) and the reduced precursor decomposition power of the reactant gas during PEALD [41]. Because the TiO\(_{1.70}\) film was not sufficiently crystallized and possessed nano-sized crystallites in the amorphous matrix, diffraction peaks for the crystalline TiO\(_2\) phase were hardly observed in the XRD curves.

For detailed investigation of the microstructure of the PEALD TiO\(_x\) film, Raman spectroscopy was performed because it provides information on TiO\(_x\) even at sub-10 nm

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Figure 1. Cross-sectional TEM micrographs of PEALD TiO\textsubscript{x} films: ((a), (b)) TiO\textsubscript{1.62} and ((c), (d)) TiO\textsubscript{1.70}. The nanocrystallites in the TiO\textsubscript{1.70} film are indicated by dotted lines in (d).

Figure 2. The evolution of Raman spectra of PEALD TiO\textsubscript{x} films with different x. Unlike the XRD results, in which no diffraction peaks of crystalline phase were observed for any of the TiO\textsubscript{x} films with different x, it was found from Raman analyses that the TiO\textsubscript{1.70} and TiO\textsubscript{1.68} films possess the anatase phase [43, 44]. Accordingly, the nanocrystallites observed in the TEM images are responsible for the appearance of the anatase Raman mode for the TiO\textsubscript{1.70} film. Meanwhile, TiO\textsubscript{1.65} and TiO\textsubscript{1.62} exhibit the amorphous characteristic in their Raman spectra, consistently with the XRD result [45].

The growth of the non-stoichiometric TiO\textsubscript{x} films could be further confirmed by confocal Raman analysis. Changes of intensity, width, and position of peaks were observed in a comparison of the Raman spectra of the TiO\textsubscript{1.70} and TiO\textsubscript{1.68} films. For the case of the $E_g$ ($\nu_6$) Raman mode, arising from the external vibration of the anatase structure, the peak position and full width at half maximum (FWHM) were 144.60 and 25.94 cm$^{-1}$ for TiO\textsubscript{1.70} and 145.56 and 75.83 cm$^{-1}$ for TiO\textsubscript{1.68}, respectively. This result is consistent with previous works, reporting that the peak position of the $E_g$ ($\nu_6$) Raman mode moves toward high frequency and the peak width increases with decrease of the x value in TiO\textsubscript{x} [46, 47]. The reduced peak intensity and broader peak
Figure 3. O 1s core-level XPS spectra of PEALD TiO$_x$ films with different $x$. The O 1s spectra were deconvoluted into two well-resolved contributions, one due to the lattice oxygen (LO) at around 529.7 eV and the other to the non-lattice oxygen (NLO) at around 531.1 eV. The peaks for LO and NLO were normalized with respect to the maximum peak intensity of the simulated fits.

The XPS binding energies of the TiO$_x$ films are affected by the presence of the non-lattice oxygen (NLO), indicating the existence of oxygen vacancies ($V_0$) [48, 49]. To investigate not only the chemical and electronic structure but also the presence of oxygen vacancies ($V_0$) in our TiO$_x$ films, the XPS spectra of N 1s and O 1s were analyzed. For all of our oxide films, we could not detect any nitrogen related XPS core-level signals (see figure S3 available at stacks.iop.org/Nano/24/295202/mmedia). This result indicates that incorporation of nitrogen into the oxide films does not occur under our PEALD conditions, irrespective of $R_F$. We assume that the nitrogen in our reactant mixture (i.e., O$_2$ + N$_2$) does not participate in the decomposition reaction of the precursor (i.e., TTIP), but controls the precursor decomposition power by its relative proportion in the mixture.

Figure 3 shows the XPS core-level spectra of O 1s for PEALD TiO$_x$ films with different $x$. From the peak deconvolution analysis, the electron binding energies for lattice oxygen (LO) in stoichiometric TiO$_2$ and for non-lattice oxygen (NLO) in oxygen deficient TiO$_x$ ($x < 2.00$) were estimated to be 529.7 eV and 531.1 eV, respectively. Figure 4 shows the change of NLO content in the oxide film as a function of $R_F$. The change of $x$ in TiO$_x$ is also shown in the figure to help in understanding the relation between $x$ and NLO content. It is evident from the figure that the NLO content in PEALD TiO$_x$ film decreases systematically as the precursor decomposition power of the reactant (i.e., $R_F$) increases. The amount of oxygen vacancies ($V_0$) is proportional to the NLO content [33, 48]. Therefore, it is immediately apparent from the figure that the amount of oxygen vacancies ($V_0$) decreases with the precursor decomposition power (i.e., $R_F$).

3.3. Spectroscopic characterization of the oxygen vacancies ($V_0$)

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Figure 5. SE results for PEALD TiO$_x$ films with different $x$. (a) Refractive indices ($n$) as a function of wavelength ($\lambda$). The inset presents refractive indices at $\lambda = 580$ nm. (b) Absorption coefficients ($\alpha$) as a function of photon energy. The inset shows the SE ratio of absorption from the defect states to that from the conduction band (CB) states as a function of $x$. (c) Wemple–DiDomenico dispersion relations for TiO$_x$ films with different $x$; the solid lines are the linear fits to the respective dispersion relations. (d) The evolution of coordination number ($N_c$) as a function of $x$ in TiO$_x$ films.

The optical properties including refractive index ($n$) and absorption coefficient ($\alpha$) were investigated by SE to gain information about the defect states of our TiO$_x$ films [50]. Parameterization of the refractive index ($n$) may supply additional information on the coordination number ($N_c$) of the titanium cation [51]. Figure 5 presents a summary of the SE analyses on the PEALD TiO$_x$ films. The refractive index ($n$) of the TiO$_x$ film increased with $x$ within the range of wavelength ($\lambda = 200–1000$ nm) for ellipsometry measurements, as shown in figure 5(a). The refractive index ($n_{\lambda=580\text{ nm}}$) determined at $\lambda = 580$ nm was in the range of 2.469–2.486, which is typical for oxygen deficient titanium oxide [52, 53]. Based on this result, we assumed that TiO$_x$ films with higher $x$ values are denser compared to those with smaller $x$ values. This assumption could be verified by the in-depth analyses on SE data. Figure 5(b) shows the absorption coefficients ($\alpha$) of PEALD TiO$_x$ films as a function of photon energy. The absorption at photon energies below 3.34 eV originates from the absorption by the defect state, while the absorption above 3.34 eV comes from the absorption by the conduction band (CB) state. Absorption ratios (defined by the SE ratios) of the defect states to the CB states were determined according to the method reported previously [50]. The inset of figure 5(b) shows the SE ratios as a function of $x$ values in TiO$_x$.

The bandgap energies ($E_g$) of TiO$_x$ samples with different $x$ were extracted by extrapolation of the Tauc plot (supplementary data figure S4 available at stacks.iop.org/Nano/24/295202/mmedia). The bandgap energies ($E_g$) of our TiO$_x$ samples turned out to be 3.34 eV irrespective of $x$ in TiO$_x$. As shown in figure 5(b), TiO$_x$ films with smaller $x$ exhibited more absorption from the defect states, indicating the larger amount of oxygen vacancies (V$_O$) for more oxygen deficient TiO$_x$ films. It is evident from this result that the TiO$_x$ films grown at smaller $R_F$ have larger amounts of vacancy-induced defect states below $E_g$, which is in good agreement with a previous report on infrared (IR) absorption of reduced rutile TiO$_2$ single crystals [54]. Based on the ellipsometry results, the observed positive correlation between the refractive index ($n$) and $x$ (see figure 5(a))

\[
\alpha = \frac{4\pi k}{\lambda}.
\]
can be ascribed to the decrease in the amount of oxygen vacancies \( (V_{O}) \) with increase in \( x \). This relation could be further supported by analyzing the coordination number \( (N_{c}) \) of the titanium cation in the TiO\(_{x}\) films. In order to determine the coordination number \( (N_{c}) \), we parameterized the refractive index \( (n) \) according to the one oscillator Wemple–DiDomenico (WD) model [51, 55]:

\[
n^2 - 1 = E_d E_0 / [E_0^2 - (h\nu)^2] \tag{2}
\]

where \( E_0 \) is the single oscillator energy, \( E_d \) is the dispersion energy, and \( h\nu \) is the photon energy. Figure 5(c) shows the curves of the refractive index factor, \( (n^2 - 1)^{-1} \), versus \( (h\nu)^2 \). From the slope \( (1/E_0 E_d) \) and the intercept \( (E_0/E_d) \) of the linear fits of the curves, we were able to determine the single oscillator energy \( (E_0) \) and the dispersion energy \( (E_d) \), respectively. The dispersion energy \( (E_d) \) obeys the following empirical relationship [51, 55]:

\[
E_d = \beta N_c Z_n N_e \tag{3}
\]

where \( \beta \) is a constant representing the nature of chemical bonds, for which the value is 0.26 ± 0.004 eV for most oxides including TiO\(_{2}\), the coordination number \( (N_c) \) is the coordination number of the cations that are the nearest neighbors to the anion, \( Z_n \) is the formal chemical valence of the anion, and \( N_e \) is the effective number of valence electrons per anion. The coordination number \( (N_c) \) of each of the PEALD TiO\(_{x}\) films was obtained from equation (3) and the values of \( Z_n \) and \( N_e \) are 2 and 8 for TiO\(_{2}\), respectively [51]. As shown in figure 5(d), \( N_c \) monotonically increases from 5.30 to 5.42 as \( x \) increases from 1.62 to 1.70, and is smaller than that \( (N_c = 6) \) of the six-coordinated stoichiometric TiO\(_{2}\) [51]. The results of ellipsometry offer additional evidence on the increase in the amount of oxygen vacancies \( (V_{O}) \) and degradation in crystallinity for more oxygen deficient TiO\(_{x}\) films, namely, those with smaller \( x \) values.

3.4. Effect of \( V_{O} \) concentration on RS behavior

As mentioned earlier, the formation and rupture of the conduction paths with oxygen deficient Magnéli phase \( (\text{Ti}_6\text{O}_{22–x}) \) under an electrical stimulus are responsible for the RS behavior of TiO\(_{2}\)-based devices [12, 13, 15]. The evolution of the conducting Magnéli phase \( (\text{Ti}_6\text{O}_{22–x}) \) originates from the migration and ordering of the oxygen vacancies \( (V_{O}) \) within a TiO\(_{2}\) film [13, 15]. Thus, the concentration of the oxygen vacancies \( (V_{O}) \) in TiO\(_{x}\) films would affect the RS behavior of our Pt/TiO\(_{x}\)/Pt devices.

The RS behavior of Pt/TiO\(_{x}\)/Pt capacitors was investigated by measuring the current–voltage \( (I–V) \) curves. Regardless of the \( x \) values in TiO\(_{x}\), the capacitors were electroformed within the voltage range of 9.0–14.0 V. To prevent permanent breakdown of the capacitors, the current compliance was set at 10 mA during the electroforming. Figure 6 presents the \( I–V \) curves of Pt/TiO\(_{x}\)/Pt capacitors with \( x = 1.62, 1.65, 1.68, \) and 1.70 for ten repetitive switching cycles; after being electroformed, the capacitors exhibited typical unipolar resistive switching (URS) behavior. As shown in figure 6, two different drastic current changes were observed in the \( I–V \) curves. Abrupt current rises occurred during the SET switching from HRS to LRS. On the other hand, sudden current drops took place during the RESET switching from HRS to LRS.

Figure 7 is a representative double-logarithmic plot of an \( I–V \) curve of a Pt/TiO\(_{1.70}\)/Pt capacitor for one switching cycle. As shown in figure 7, the \( I–V \) curves at LRS are well described by the Ohmic conduction behavior \( (I \propto V) \) by dint of the conducting paths between the top Pt electrode and the bottom Pt electrode. On the other hand, the electrical conduction for HRS is described by the trap-controlled space-charge-limited conduction (SCLC) mechanism as follows [56–59]. In region I of the low voltage range \( (V < V_{SCL}) \), the \( I–V \) curves follow Ohm’s law \( (I \propto V) \) because the thermally generated free carrier density \( (n_0) \) governs the conduction; the density of injected charge carriers is lower than that of thermally generated free carriers. With increasing voltage, the injected carriers dominate the conduction and a quadratic \( I–V \) relation \( (I \propto V^2) \) is observed in the intermediate voltage region \( (\text{region II}; V_{SCL} < V < V_{TFL}) \). The voltage required for the transition from the Ohmic (i.e., region I) to the space-charge-limited regime (i.e., region II) is defined as \( V_{SCL} \). The observed \( I–V \) characteristics in region II can be explained by the space-charge-limited conduction (SCLC). As the applied voltage bias is increased far above \( V_{SCL} \), all the traps will be filled with the injected carriers. Under such conditions, a drastic current jump should occur at \( V_{TFL} \). In real systems, however, the current increases with a finite slope \( (I \propto V^l) \), where the value of \( l \) is larger than 2) due to the distribution of the energy states of traps as in region III \( (V > V_{TFL}) \) of figure 7. The current densities in regions I (\( J_I \)) and II (\( J_{II} \)) can be described by the equations given below [57]:

\[
J_I = q \mu n_0 V / d \tag{4}
\]

\[
J_{II} = 9 / 8 \varepsilon_0 \varepsilon_r \mu_0 V^2 / d^3 \tag{5}
\]

where \( q \) is the electron charge, \( \mu \) is the electron mobility, \( V \) is the applied voltage, \( d \) is the switching layer thickness, \( \varepsilon_0 \) is the relative dielectric constant of the switching layers, \( \varepsilon_r \) is the vacuum permittivity and \( \theta \) is the ratio of the free to the trapped carrier concentration. The \( I–V \) curves for HRS are described according to the trap-controlled SCLC mechanism based on the fitting results for each voltage region, as shown in figure 7 by the double-logarithmic \( I–V \) curves of the Pt/TiO\(_{x}\)/Pt capacitors. The conduction behavior at HRS of Pt/TiO\(_{x}\)/Pt capacitors with \( x = 1.62, 1.65, \) and 1.68 also follows the trap-controlled SCLC mechanism (see also figure S5 available at stacks.iop.org/Nano/24/295202/mmedia).

Figure 8 shows the results of statistical analyses on the \( I–V \) curves of Pt/TiO\(_{x}\)/Pt capacitors. The resistances at the as-prepared state \( (R_{As-prep}) \) and HRS \( (R_{HRS}) \) increased monotonically with \( x \) in TiO\(_{x}\) as shown in the distribution of both resistances of figure 8(a). These observed switching characteristics can be ascribed to increase in the electrical conductivity of TiO\(_{x}\) films with the decrease of \( x \), namely, increase of the oxygen vacancy \( (V_{O}) \) concentration. On the other hand, the increase in SET voltage \( (V_{SET}) \) with increasing
Figure 6. $I$–$V$ curves of Pt/TiO$_x$/Pt capacitors: (a) $x = 1.62$, (b) $x = 1.65$, (c) $x = 1.68$, and (d) $x = 1.70$. The inset in (a) is a schematic illustration of the capacitor.

$x$ values (the blue box trace in figure 8(b)) can be explained by the effect of oxygen vacancies ($V_O$) on the transition from HRS to LRS. A higher $V_O$ concentration in TiO$_x$ films facilitates the recovery of CFs that were ruptured during the preceding RESET cycle, the rejuvenation of CFs arising from the migration and ordering of the oxygen vacancies ($V_O$) [13, 15]. Correspondingly, TiO$_x$ films with larger amounts of oxygen vacancies ($V_O$) can be expected to undergo abrupt current jumps at lower voltages ($V_{SET}$) than those with smaller amounts of oxygen vacancies ($V_O$). Meanwhile, the RESET voltages ($V_{RESET}$) were found to be independent of the $x$ values in TiO$_x$ (the red box trace in figure 8(b)). This experimental observation reveals that there is no direct relation between the destruction of the conducting filament (CF) and the concentration of oxygen vacancies ($V_O$).

The conduction behavior at HRS for all of the Pt/TiO$_x$/Pt capacitors was found to follow the trap-controlled SCLC mechanism (see figure S5 available at stacks.iop.org/Nano/24/295202/mmedia). The transition voltages of $V_{SCL}$ and $V_{TFL}$ were extracted by fitting analyses on the $I$–$V$ curves for HRS for capacitors with different TiO$_x$ samples. The distributions of $V_{SCL}$ and $V_{TFL}$ for the Pt/TiO$_x$/Pt capacitors are given in figure 9. As shown in the figure, both $V_{SCL}$ and $V_{TFL}$ were found to decrease with increasing $x$. It has been reported that
the densities of free carriers \(n_0\) and traps \(N_t\) are inversely proportional to the resistances in the Ohmic regime \([60]\).

Accordingly, we can relate the densities of free carriers \(n_0\) and traps \(N_t\) with \(V_{SCL}\) and \(V_{TFL}\). The HRS resistances shown in figure 8(b) were read at 0.1 V, which corresponds to a voltage value in the Ohmic region (i.e., below \(V_{SCL}\)). The larger the \(x\) values in TiO\(_x\) are, the higher the resistances in the Ohmic regime for the Pt/TiO\(_x\)/Pt capacitors are. This indicates that the densities of free carriers \(n_0\) and traps \(N_t\) increase with decreasing \(x\) values. Correspondingly, Pt/TiO\(_x\)/Pt capacitors with smaller \(x\) values need higher voltages of \(V_{SCL}\) to enter the space-charge-limited state and to experience drastic current rise at \(V_{TFL}\); higher \(V_{SCL}\) and \(V_{TFL}\) for TiO\(_x\) with smaller \(x\) arise from higher \(V_O\) concentration. All of these results on the \(I−V\) characteristics of Pt/TiO\(_x\)/Pt with different \(x\) show that the concentration of oxygen vacancies \(V_O\) in TiO\(_x\) films plays an important role in governing the RS behavior of Pt/TiO\(_x\)/Pt capacitors as well as the conduction characteristics that can be described by the trap-controlled SCLC model.

### 4. Conclusions

The stoichiometry of TiO\(_x\) films was readily controlled by plasma-enhanced atomic layer deposition (PEALD) under precisely controlled precursor decomposition power \(R_F\) of the plasma-activated reactant mixture \((\text{N}_2 + \text{O}_2)\), as confirmed by Rutherford backscattering spectrometry (RBS). Based on the various spectroscopic and microstructural analyses by using Rutherford backscattering spectrometry (RBS), x-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy, confocal Raman spectroscopy, and spectroscopic ellipsometry (SE), \(R_F\) during PEALD was revealed to govern not only the oxygen vacancy concentration but also the crystallinity of the resulting TiO\(_x\) film: nanocrystalline anatase TiO\(_x\) with fewer oxygen vacancies under high \(R_F\), while amorphous TiO\(_x\) with more oxygen vacancies under low \(R_F\). Enabled by our controlling capability over the \(V_O\) concentration, we were able to thoroughly elucidate the effect of \(V_O\) on the RS behavior of TiO\(_x\)-based capacitors with different \(x\). Our capacitors exhibited typical unipolar RS (URS) behavior. We found that the SET voltage \(V_{SET}\) required for the transition from high resistance state (HRS) to low resistance state (LRS) decreases with the amount of \(V_O\) in the oxide layer, whereas the RESET voltage \(V_{RESET}\) was found to be independent of the \(V_O\) content. The current–voltage \((I−V)\) relation at HRS was characterized by three distinct regimes, which can be explained by the trap-controlled space-charge-limited conduction (SCLC) with two characteristic transition voltages. One is the voltage \(V_{SCL}\) for the transition from Ohmic conduction to space-charge-limited conduction (SCLC) with two characteristic transition voltages. In this work, we disclosed for the first time the dependence of these two characteristic transition voltages (i.e., \(V_{SCL}\) and \(V_{TFL}\)) on the \(V_O\) concentration. This research provides insight into the importance of \(V_O\) not only for the...
electrical properties of TiO$_2$ materials but also for the RS behavior of TiO$_2$-based resistive memory capacitors. Apart from ReRAM applications, our approach for tight control of $V_{th}$ and results will prove to be useful in the development of oxide-based high performance sensors, catalysts, and energy storage/conversion devices, in which the concentration of oxygen vacancies is important.

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