Electroforming free resistive switching memory in two-dimensional VOx nanosheets

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Citation: [Applied Physics Letters](#) **107**, 163106 (2015); doi: 10.1063/1.4933335

View online: <http://dx.doi.org/10.1063/1.4933335>

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Electroforming free resistive switching memory in two-dimensional VO_x nanosheets

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(Received 17 May 2015; accepted 6 October 2015; published online 21 October 2015)

We report two-dimensional VO_x nanosheets containing multi-oxidation states (V⁵⁺, V⁴⁺, and V³⁺), prepared by a hydrothermal process for potential applications in resistive switching devices. The experimental results demonstrate a highly reproducible, electroforming-free, low SET bias bipolar resistive switching memory performance with endurance for more than 100 cycles maintaining OFF/ON ratio of ~ 60 times. These devices show better memory performance as compared to previously reported VO_x thin film based devices. The memory mechanism in VO_x is proposed to be originated from the migration of oxygen vacancies/ions, an influence of the bottom electrode and existence of multi-oxidation states. © 2015 AIP Publishing LLC.
[\[http://dx.doi.org/10.1063/1.4933335\]](http://dx.doi.org/10.1063/1.4933335)

Two-dimensional (2D) nanomaterials (particularly nanosheets), such as graphene, transition metal dichalcogenide nanosheets (e.g., MoS₂, WS₂, TiS₂, TaS₂, single layers of boron nitride *etc.*) and transition metal oxides (e.g., MoO₃, VO₂, V₂O₃, V₂O₅ *etc.*) have attracted increasing attention in recent years, due to their 2D morphology, exceptionally high specific surface area and potential applications in electronics.^{1–4} Among layered oxides, vanadium oxide is one of the most extensively studied binary oxides due to its rich variety of vanadium/oxygen stoichiometries and characteristic properties of the individual phases (such as V₂O₅, VO₂, V₂O₃, V₆O₁₃ *etc.*). This has resulted in many studies targeting the use of vanadium oxide in various applications such as energy storage,^{5,6} catalysis,⁷ electrochromism,⁸ sensing,⁹ and spintronic devices.¹⁰ In contrast, VO_x thin films have also been reported recently for resistive switching performance by several groups.^{11–14} However, application of VO_x 2D nanosheets in resistive switching memory devices is not yet reported. Hence, it is important to study the resistive switching property of this important 2D oxide in details.

Vanadium oxide phases can be synthesized by several methods such as wet chemical techniques,¹⁵ pulsed laser deposition,¹⁶ and sputtering or physical vapor deposition.^{11,13,17} Recently, hydrothermal approaches to synthesize VO_x has attracted the attention of the scientific community, specially synthesis in different morphologies, including nano-fibers,¹⁸ nano-rods,¹⁹ nano-belts,²⁰ nano-tubes,²¹ nano-wires,²² and nanosheets.²³

Herein, VO_x 2D nanosheets (the compound of V₂O₅, VO₂, and V₂O₃) were chemically synthesized via a hydrothermal route. Details of the experimental procedure are given in the supplementary material.⁴⁹ The Raman spectra were measured at room temperature using a 532 nm laser source and are shown in Fig. 1(a). The nanosheets are found to be mixed phases of VO₂, V₂O₅, and V₂O₃.^{24–27} The peaks at 283 and 404 cm^{–1} can be attributed to the bending and stretching vibrations of the bridge-sharing V–O band,

respectively, while the band around 694 cm^{–1} comes from the stretching of V₂–O.²⁶ Figure 1(b) shows high-resolution transmission electron microscopy (TEM) image from the VO_x nanosheets. It is clearly observed that nanosheets are formed with lattice fringes with a spacing of 0.284 nm, corresponding to the (1 1 1) planes of V₂O₅.

To check the chemical composition, X-ray photoelectron spectroscopy (XPS) analysis was carried out. The binding energies were corrected with reference to O 1s at 530.0 eV, instead of the usual C 1s, as O 1s is a better energy reference for the V 2p binding energies of vanadium oxides due to the presence of high numbers of oxidation states of Vanadium.²⁸ Furthermore, the difference in binding energy (Δ) between the O 1s and V 2p_{3/2} level was used to determine the oxidation state of the vanadium. Figure 1(c) shows the XPS analysis of V 2p core level spectra obtained from the VO_x nanosheets. The major peaks in V 2p_{3/2} and V 2p_{1/2} are centered at 517.13 and 524.46 eV, respectively. The binding energy difference

FIG. 1. (a) Raman study obtained from VO_x nanosheets. (b) Hi-resolution TEM image shows the formation of nanosheets. XPS spectra of (c) V 2p, (d) O 1s, and (e) C 1s. XPS analysis confirmed that the nanosheets consist of different oxidation phases of Vanadium, such as V⁵⁺, V⁴⁺, and V³⁺.

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(Δ) between O 1s and V $2p_{3/2}$ level was found to be ~ 12.87 eV. The values for the peak center and the binding energy difference indicate the presence of V^{5+} phase.²⁹ In addition, from V $2p_{3/2}$ curve fitting, V^{4+} and V^{3+} states were also identified at 516.1 and 515.29 eV, respectively.²⁸ The O 1s spectrum can also be deconvoluted into three peaks, as shown in Fig. 1(d). The peak position at a binding energy of 530 eV may be attributed from the O^{2-} ions surrounded by the V atoms, i.e., from the V-O bonds. The peaks at 530.9 and 532.2 eV may be due to the presence of C=O and C-O(H) bonds, respectively.³⁰ The presence of C=O and C-O (H) bonds were further confirmed from the C 1s deconvolution spectra at 285.46 and 288.03 eV, respectively, as shown in Fig. 1(e). The XPS analysis of VO_x nanosheets reveals that multi-oxidation states, mainly, V^{5+} , V^{4+} , and V^{3+} exists in the VO_x nanosheets.

The memory performance obtained in VO_x nanosheets was studied using ITO and Au as bottom and top electrode, respectively. The voltage was applied in a sequence: $0 \rightarrow -V_{\max} \rightarrow 0 \rightarrow +V_{\max} \rightarrow 0$. After few initial unstable voltage sweeping cycles (see the supplementary material⁴⁹), stable bipolar resistive switching characteristics were observed (as shown in Fig. 2(a)). The switching from high resistance state (HRS) to low resistance state (LRS) occurs at ~ -0.5 V (called “SET,” i.e., ON state), and that from LRS to HRS appears at $\sim +2.3$ V (called “RESET” i.e., OFF state). It should be noted that the resistive switching performance was achieved without applying any electroforming voltage or pulse, which means a self-electroforming process has occurred during the dc voltage sweeping cycles. This behavior is attractive because it simplifies memory operation and enables the fabrication of higher density memory devices. On the other hand, no current compliance limit was also applied during the switching cycles, which signifies the advantage (e.g.,

self-compliance effect) of this device to be used without an external current limiter to protect the device from hard breakdown.³¹

Next, to understand the electrode effect, the memory performance was investigated with VO_x nanosheets in Au/ VO_x /Au and Al/ VO_x /Au device structure, as shown in Figs. 2(b) and 2(c), respectively. It is found that the resistive switching effect with Au and Al, as bottom electrodes, is not significant, which suggests that the bottom electrode plays an important role in the resistive switching performance.

The endurance characteristics of our nanosheet based memory devices were evaluated. The endurance performance obtained from ITO/ VO_x /Au device structure is shown in Fig. 2(d). The HRS and LRS for each cycle (total 122 cycles) were extracted from the corresponding current-voltage curve at $V = 0.25$ V (read voltage). Two distinct resistance states can be observed throughout the endurance test. However, a fluctuation in the HRS was observed while LRS remained stable. This type of endurance performance suggests that different amount of “residual or tiny filaments” may exist in the HRS state during dc switching cycles.³² Indeed, an average switching ratio of ~ 60 times (sufficient to separate the ON/OFF states) is maintained during the whole switching operation (note that a minimum resistance ratio of $HRS/LRS > 10$ is required for highly efficient memory cell³³). In addition, the retention characteristics were also studied and indicated a stable memory performance (see the supplementary material⁴⁹). Furthermore, it was observed that the average SET voltage is around -0.42 V, while the average RESET voltage is about 2.26 V during the DC sweeping cycles, as shown inset of Fig. 2(d). This low value of SET voltages can be explained by the enhanced formation process of conducting filaments in the presence of ITO as the bottom electrode, and by multi-oxidation states exist in VO_x nanosheets (details mechanism will be discussed later). As

FIG. 2. Hysteretic current-voltage characteristics obtained from (a) ITO/ VO_x /Au, (b) Au/ VO_x /Au, and (c) Al/ VO_x /Au memory device structures. (d) Endurance study in ITO/ VO_x /Au memory device structure and SET and RESET voltage variation during DC cycles (inset).

compared to thin film VO_x based resistive switching devices reported by several research groups,^{11,13,34} our VO_x nanosheet devices show better performance in terms of (i) electroforming-free resistive switching performance, (ii) low SET bias, and (iii) better DC cyclic stability. This advantage of using nanosheets is very useful for making low power resistive switching memory devices. A comparison of several important electrical parameters of VO_x based resistive switching devices with VO_x as thin film and nanosheets is shown in tabular format, Table S1 (see the supplementary material⁴⁹).

To understand the resistive switching process, the conduction mechanism of the memory device was studied at different temperatures for both LRS and HRS in positive and negative polarity. The resistive switching characteristics of the ITO/ VO_x /Au memory structure measured at different temperatures ranging from 300 to 380 K is shown in Fig. 3(a). It is observed that the LRS resistance was almost independent (slightly increasing) while the resistance of the HRS decreases gradually with increasing temperature (see Fig. S5 in the supplementary material⁴⁹). These results indicate the semiconducting or oxide like nature of the nanosheets during HRS, while LRS indicates the existence of metallic-like conduction.^{35,36} To further investigate the conduction mechanism, the temperature dependent current-voltage characteristics were re-plotted in log-log scale as shown in Figs. 3(b)–3(e). It can be observed that the HRS current-voltage characteristics have four distinguished regions, denoted as I, II, III, and IV in the negative polarity side (Fig. 3(b)). The low bias region (varying from 0 to -0.3 V for the temperature range of 300 to 360 K and 0 to -0.35 V for 380 K) shows Ohmic behavior as the slope of $\ln |I|$ versus $\ln |V|$ is close to unity (denoted as “I”). This might be due to the existence of electric field dependent thermally generated free carriers at low bias application.^{37,38} In region-II (varying

from -0.3 to -0.35 V for the temperature range of 300 to 360 K and -0.35 to -0.45 V for 380 K), the current increases rapidly with the applied bias and a certain jump in the current order was found (slope > 2). This may be due to the rapid increase of injected electrons with increasing bias. Few of the injected electrons might be trapped in different traps (mainly oxygen vacancies) present in the VO_x nanosheets and others will contribute to the total current. This is recognized as the charge injection limited and trap filling region.³⁹ After filling all the traps, the injecting carriers start to form space charge near the injecting electrode with increasing applied bias (denoted as region-III with slope ~ 2). This region may be recognized as trap-free (since all traps are filled) space charge limited current conduction region. However, an interesting characteristic was observed for the higher voltage region (beyond -0.75 V) for all temperature that the current again starts to follow a linear relationship with the applied voltage ($V \propto I$) i.e., it become Ohmic (denoted as “IV”) again. This signifies the full transition of HRS to LRS at higher negative bias. Next, the current conduction process for the LRS state in both negative and positive polarity shows Ohmic type as current varied linearly with the applied voltage (i.e., $V \propto I$) for all temperatures, as shown in Figs. 3(c) and 3(d), respectively. However, the HRS in positive polarity side shows three different types of conduction process, as shown in Fig. 3(e). In the low voltage region (< 0.4 V) of HRS state (denoted as “A”), the slope of the linear fit is found to be ~ 1 i.e., $I \propto V$, which implies Ohmic conduction process. However, the current shows a non-linear relationship with the applied voltage in higher voltage region. The slope of the curve fitting results in the bias range between 0.5 to 1.06 V (for the temperature range from 300 to 340 K) and 0.5 to 1.5 V (for the temperature range from 360 to 380 K) was found to vary from 1.3 to 1.7. This type of conduction might be from the Poole-Frenkel

FIG. 3. (a) Hysteretic current-voltage characteristics with different measurement temperatures. Current conduction process for (b) negative bias HRS, (c) negative bias LRS, (d) positive bias LRS, and (e) positive bias HRS. (f) PF conduction with different temperatures.

(PF) emission process.⁴⁰ To check the PF process in this region, $\ln(I/V)$ was plotted against $V^{1/2}$ and a linear relationship was obtained for all the measurement temperatures, which reveals that the current conduction is dominated by PF emission,⁴¹ as shown in Fig. 3(f). However, for the higher bias range (denoted as “C”), the slope of the fittings is found to vary from 2 to 2.58 for different temperature range, indicating the co-existence of trap filling and trap-free space charge conduction process, like in HRS for negative polarity side, as mentioned above. Hence, the cyclic transition of the above-mentioned conduction process seems to be the origin of resistive switching in the VO_x nanosheet memory devices.

In light of the material analysis and electrical results described above, a resistive switching mechanism in ITO/VO_x/Au memory structure has been proposed, the sketches of which are depicted in Fig. 4. For a multi-valency material like vanadium oxide, it is expected that the oxygen vacancies (positively charged, V_O^{2+}) or ions might be generated due to the decomposition of higher oxidation states of vanadium into its lower oxidation states during the applied voltage sweep.^{42,43} In contrast, additional oxygen vacancies are possible in multi-layer VO_x nanosheets multi-layer structure. Each individual nanosheet will generate additional oxygen vacancies at or near the surface of the individual oxide nanosheets, due to the lower energy required for the formation of oxygen vacancies at or near the surface.⁴⁴ As a result, it is highly possible that the multi-layer nanosheets of thickness ~ 25 nm (several layers) must consist of a considerable amount of oxygen vacancies. It is also expected that the drift motion of oxygen ions or vacancies will be enhanced due to the existence of different oxidation phases (e.g., V₂O₅, VO₂, and V₂O₃) in the VO_x nanosheets. These various states can facilitate the formation of conducting filaments inside the nanosheets. Regarding the role of the bottom electrode in the resistive switching process, Yang *et al.* reported that ITO can act as a source or reservoir of oxygen ions (O^{2-}) and

oxygen vacancies.⁴⁵ Hence, under the application of negative bias on the top electrode, a drift of O^{2-} towards the bottom electrode (ITO) can be expected. Simultaneously, the drift of positive ions, such as V_O^{2+} , may take place towards the top electrode, and they accumulate near the top electrode-oxide interface. When the applied voltage reaches SET voltage range, a conductive path forms from top to the bottom electrode. As soon as this path forms, the electrons from the top electrode start moving through this path like in a metallic wire (Fig. 4(a)). However, not only V_O^{2+} but also the active Sn^{4+} ions in ITO have been suggested to play an important role in the resistive switching process.⁴⁶ Under the application of the negative bias on the top electrode, a drift motion of Sn^{4+} ions from ITO to the VO_x nanosheets is expected, where they may partially react with O^{2-} , would form the Sn^{2+} ions ($Sn^{4+} + O^{2-} \rightarrow Sn^{2+} + O_0$, where O_0 is the neutral oxygen molecule). It is conjectured that these Sn^{2+} ions along with O^{2-} ions may form an interfacial layer near the bottom electrode, which forms an internal resistance resulting in self-compliance effect in the current-voltage characteristics.^{47,48} The reaction process of Sn^{4+} with O^{2-} enhances the O^{2-} absorption process into ITO, resulting in the enhancement of V_O^{2+} generation process in VO_x nanosheets. These effects ultimately lead to a low voltage SET process in these devices. However, during the application of positive bias on the top electrode, O^{2-} ions start drifting from the ITO and recombine with few V_O^{2+} , resulting in rupture process of the conducting filaments. The remaining V_O^{2+} move towards the bottom electrode, which enhances the rupture process of the conducting filaments. As a consequence of the rupture process of the conducting filaments, the memory device is again RESET back to its HRS condition (Fig. 4(b)). However, during this rupture process, it is possible that different conducting filaments may rupture at various times or may partially break (resulting in “tiny filaments”), leading to the fluctuation of the current level in the HRS state.

In summary, electroforming-free and self-compliance based bipolar resistive switching behavior has been demonstrated in VO_x 2D nanosheets. By using ITO as the bottom electrode, a reasonable and repeatable resistive switching memory performance was achieved. The charge transport process was governed by Ohmic behavior in LRS while HRS was dominated by multi-charge transport process. The origin of the resistive switching process in these previously unreported VO_x nanosheets is proposed to be the migration of oxygen vacancies assisted by the bottom electrode and multi-oxidation phase of V.

Research reported in this publication was supported by King Abdullah University of Science and Technology (KAUST).

FIG. 4. Schematic representation of the resistive switching process in ITO/VO_x/Au memory device structure during (a) SET and (b) RESET process.

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- ⁴⁹See supplementary material at <http://dx.doi.org/10.1063/1.4933335> for VO_x synthesis process, performance comparison of different reported VO_x memory devices, additional material, and electrical characteristics.