Electroforming free resistive switching memory in two-dimensional VOx nanosheets

Citation: Applied Physics Letters 107, 163106 (2015); doi: 10.1063/1.4933335
View online: http://dx.doi.org/10.1063/1.4933335
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/107/16?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Electroforming-free resistive switching memory effect in transparent p-type tin monoxide

Highly uniform bipolar resistive switching characteristics in TiO2/BaTiO3/TiO2 multilayer

Two resistive switching regimes in thin film manganite memory devices on silicon

Nonpolar resistive switching in Mn-doped BiFeO3 thin films by chemical solution deposition

Two-dimensional current percolation in nanocrystalline vanadium dioxide films
Electroforming free resistive switching memory in two-dimensional VOₓ nanosheets


Materials Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

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

We report two-dimensional VOₓ nanosheets containing multi-oxidation states (V^{5+}, V^{4+}, and V^{3+}), 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 VOₓ thin film based devices. The memory mechanism in VOₓ is proposed to be originated from the migration of oxygen vacancies/ions, an influence of the bottom electrode and existence of multi-oxidation states.

Copyright 2015 AIP Publishing LLC.

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, V₂O₅, V₂O₃ etc.) have attracted increasing attention in recent years, due to their 2D morphology, exceptionally high specific surface area and potential applications in electronics.

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, catalysis, electrochromism, sensing, and spintronic devices.

In contrast, VOₓ thin films have also been reported recently for resistive switching performance by several groups. However, application of VOₓ 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, pulsed laser deposition, and sputtering or physical vapor deposition. Recently, hydrothermal approaches to synthesize VOₓ has attracted the attention of the scientific community, especially synthesis in different morphologies, including nano-fibers, nano-rods, nano-belts, nano-tubes, and nanosheets.

Herein, VOₓ 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. 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, V₂O₃, and V₂O₅. 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. Figure 1(b) shows high-resolution transmission electron microscopy (TEM) image from the VOₓ 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.

Furthermore, the difference in binding energy (Δ) between the O 1s and V 2p₃/₂ 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 VOₓ nanosheets. The major peaks in V 2p₃/₂ and V 2p₁/₂ are centered at 517.13 and 524.46 eV, respectively. The binding energy difference

---

(a) Raman study obtained from VOₓ 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 V^{5+}, V^{4+}, and V^{3+}.

---

E-mail: husam.alshareef@kaust.edu.sa
(Δ) between O 1s and V 2p3/2 level was found to be ~12.87 eV. The values for the peak center and the binding energy difference indicate the presence of V5⁺ phase. In addition, from V 2p3/2 curve fitting, V4⁺ and V3⁺ states were also identified at 516.1 and 515.29 eV, respectively. 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 O2⁻ 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. 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 VOx nanosheets reveals that multi-oxidation states, mainly, V5⁺, V4⁺, and V3⁺ exists in the VOx nanosheets.

The memory performance obtained in VOx nanosheets was studied using ITO and Au as bottom and top electrode, respectively. The voltage was applied in a sequence: 0 → −Vmax → 0 → +Vmax → 0. After few initial unstable voltage sweeping cycles (see the supplementary material), 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 ~+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.

Next, to understand the electrode effect, the memory performance was investigated with VOx nanosheets in Au/VOx/Au and Al/VOx/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/VOx/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. 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 cell). In addition, the retention characteristics were also studied and indicated a stable memory performance (see the supplementary material). 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 VOx nanosheets (details mechanism will be discussed later).
compared to thin film VOₓ based resistive switching devices reported by several research groups, our VOₓ nano-sheet devices show better performance in terms (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 VOₓ based resistive switching devices with VOₓ as thin film and nanosheets is shown in tabular format, Table S1 (see the supplementary material).

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/VOₓ/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 material). These results indicate the semiconducting or oxide like nature of the nanosheets during HRS, while LRS indicates the existence of metallic-like conduction. 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. 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 VOₓ nanosheets and others will contribute to the total current. This is recognized as the charge injection limited and trap filling region. 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 ∝ 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 ∝ 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 ∝ 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

![Figure 3](image-url)
(PF) emission process. 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 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, \( V^{2+}_O \)) 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. 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. As a result, it is highly possible that the multi-layer nanosheets of thickness \( \sim 25 \text{ nm} \) (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., \( V_2O_5\), \( VO_2\), and \( V_2O_3\)) 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. 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 \( V^{2+}_O \), 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 \( V^{2+}_O \) but also the active \( Sn^{4+} \) ions in ITO have been suggested to play an important role in the resistive switching process. 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 (\( Sn^{4+} + O^{2-} \rightarrow Sn^{2+} + O_6 \) where \( O_6 \) 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. The reaction process of \( Sn^{4+} \) with \( O^{2-} \) enhances the \( O^{2-} \) absorption process into ITO, resulting in the enhancement of \( V^{2+}_O \) 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 \( V^{2+}_O \) resulting in rupture process of the conducting filaments. The remaining \( V^{2+}_O \) moves 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).
