Manuscript ID : JoVE61026

Title : Fabrication process and *in situ* nanostructural analysis methodology of volatile threshold switching in mixed-phased a-VOx based asymmetric crossbars

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RESPONSE TO THE REVIEWERS

Authors thanks the Editor and Reviewers for their time and constructive comments. We believe that the feedback has resulted in significant improvements in quality of the manuscript. We have revised our manuscript in line with all comments and suggestions made. We have also included additional references, discussions and clarifications. The modified and additional text in manuscript is marked in red.

Editorial comments:

Comment 1

Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues. The JoVE editor will not copy-edit your manuscript and any errors in the submitted revision may be present in the published version. Please use American English throughout.

Response

Manuscript has been updated and proofread thoroughly.

Comment 2

Please format the manuscript as: paragraph Indentation: 0 for both left and right and special: none, Line spacing: single. Please include a single line space between each step, substep and note in the protocol section. Please use Calibri 12 points.

Response

Manuscript updated as per JoVE template. All the above mentioned changes are included.

Comment 3

Please provide an email address for each author.

Response

Email address of all the authors are provided in affiliation section on lines 15-20.

Comment 4

Please rephrase the Short Abstract/Summary to clearly describe the protocol and its applications in complete sentences between 10-50 words: "Here, we present a protocol to …"

Response

The short abstract has been rephrased and updated on lines 27-31.

Comment 5

Please ensure that the long Abstract is within 150-300-word limit and clearly states the goal of the protocol.

Response

The long abstract has been revised as per the requirements on lines 35-50.

Comment 6

Unfortunately, there are a few sections of the manuscript that show significant overlap with previously published work. Though there may be a limited number of ways to describe a technique, please use original language throughout the manuscript. Please see lines: 36-39, 45-46, 54-56, 102-105, 110-113, 116-119, 246-264, 273-275.

Response

All the above sections have been revised to avoid the overlap to the best of our ability. However, there might be some overlap in representative results corresponding figure captions, which is unavoidable. With copyright permissions and appropriate citation, we believe it should be acceptable as has been communicated before.

For line 273-275, the overlap is for the facility acknowledgement. This cannot be rewritten or removed.

Comment 7

JoVE cannot publish manuscripts containing commercial language. Please remove all commercial language from your manuscript and use generic terms instead. All commercial products should be sufficiently referenced in the Table of Materials and Reagents. For example: AZ5214E photoresist, MLA150 Maskless Aligner – Heildberg

instruments, Lesker PVD75, Keithley 4200 source-meter, Linkam, JEOL 2100F, FEI Scios DualBeamTM system, Protochips, E-chips, Fusion biasing holder, etc.

Response

All the commercial language is removed from the main manuscript and all commercial products are reference in the Table of Materials and Reagents.

Comment 8

Please revise the Introduction to include all of the following with citations:

a) A clear statement of the overall goal of this method

b) The rationale behind the development and/or use of this technique

c) The advantages over alternative techniques with applicable references to previous studies

d) A description of the context of the technique in the wider body of literature

e) Information to help readers to determine whether the method is appropriate for their application

Response

The introduction section is revised to include all the above suggested points on line 51 to 95.

Comment 9.

The Protocol should contain only action items that direct the reader to do something in a stepwise manner. Please move the discussion about the protocol to the Discussion.

Comments 10

The Protocol should be made up almost entirely of discrete steps without large paragraphs of text between sections. Please ensure that individual steps of the protocol should only contain 2-3 actions per step.

Comment 11

Please make sections in the protocol to help navigate from one step to the next.

Comment 12

Please adjust the numbering of the Protocol to follow the JoVE Instructions for Authors. For example, 1 should be followed by 1.1 and then 1.1.1 and 1.1.2 if necessary. Please refrain from using bullets or dashes.

Comment 13

Please ensure that all text in the protocol section is written in the imperative tense as if telling someone how to do the technique (e.g., "Do this," "Ensure that," etc.). The actions

should be described in the imperative tense in complete sentences wherever possible. Avoid usage of phrases such as "could be," "should be," and "would be" throughout the Protocol. Any text that cannot be written in the imperative tense may be added as a "Note."

Comment 14

Please add more details to your protocol steps. Please ensure you answer the "how" question, i.e., how is the step performed? Please include discrete experimental steps, button clicks in the software, knob turns in the instruments etc.

Response

The protocol has been updated to incorporate all the comments from 9 to 14 on lines 97 to 208.

Comment 15

What kind of image was used for the study? Reference for standard image? How was the patterning performed? How was the deposition performed, what are the conditions used? How do you liftoff the patterns?

Response

We believe that the editor is referring to the fabrication process here. A standard and well known image reversal photolithography recipe was used for patterning. "Image reversal" is name of the process. The masks used for photolithography replicate the device schematic presented in Figure 10. All the details about patterning, deposition, and lift-off are included in the protocol on lines 98 to 118.

Please note that all the steps in device fabrication section, from the methodology point of view are standard. There are seven instruments used in this process. If we include all the minor details of how those 7 instruments were used in this fabrication, it will be more than 10 pages. While that is not the core idea of this paper, every lab has different set of instruments to perform standard processes and in depth explanation on how that action was performed will not be widely useful.

We have revised this section and included all the critical steps, conditions, and parameters sufficient to replicate the fabrication.

Comment 16

How was the electrical charactezation performed? Please describe the actions associated with it. What are the parameters being studied and how?

Response

We have revised this section and details are explained on lines 119 -130.

Comment 17

Lines 101-108, 110-114, 116-120, 159-160, 162-173, 178-184, 189-192, 241-242: Either make action steps or move to the intro/results/discussion wherever applicable.

Response

The updates have been included as requested. Now the protocol includes only action steps, rest of the details have been moved to discussion section.

Comment 18

Line 122: How were the samples prepared for in situ biasing experiments, condition etc?

Response

We believe the Editor is referring to the fabrication of the sample which is separately prepared for *in situ* experiment. The sample which is fabricated separately follows the same procedure as explained in fabrication procedure section on lines 98-118, with one modification which is explained on lines 150-153.

The lamella preparation and mounting on biasing chip section of the protocol explains the procedure for *in situ* lamella preparation on lines 150-153.

Comment 19

Line 143: What is the set up for Auto TEM program.

Auto TEM setup explained on lines 163-171.

Comment 20

Line 144: How is this done?

Response

The details are provided in gridbar and biasing chip mounting section on lines131-148.

Comment 21

Step 6: how was this done? Please describe all the actions.

Response

It has been explained with a note in the lamella preparation and mounting on biasing chip section on lines 197-198.

Please note that these actions are the basic operations of any electron microscope for pre-processing adjustments. The specific actions such as use of software, mouse or keyboard will change with the instrument and software. The focus of this protocol is not the preliminary focusing, astigmatism or beam alignment of focused ion beam (FIB) used in this case. The same experiment can be performed with other FIB. To target the larger audience, we believe it would be beneficial to provide critical details and conditions sufficient to replicate the experiment.

Comments 22

There is a 10-page limit for the Protocol, but there is a 2.75-page limit for filmable content. Please highlight 2.75 pages or less of the Protocol (including headings and spacing) that identifies the essential steps of the protocol for the video, i.e., the steps that should be visualized to tell the most cohesive story of the Protocol.

Response

The main protocol is highlighted in Grey color.

Comments 23

Please do not combine the results and discussion section. Please include at least one paragraph of text to explain the Representative Results in the context of the technique you have described, e.g., how do these results show the technique, suggestions about how to analyze the outcome, etc. The paragraph text should refer to all of the figures. Data from both successful and sub-optimal experiments can be included.

Response

A separate section for representative results is included in the revised manuscript on lines 210 to 237. The context of the representative results section has been revised to include all the comments from Editors.

Comment 24

Please discuss all figures in the Representative Results. However, for figures showing the experimental set-up, please reference them in the Protocol.

Response

All the Figures relevant to the representative results section (Figure 7) are discussed there. The image relating to fabrication flow and device schematics (Figure 8) is discussed in discussion section. Rest all the figures show experimental set-up and are addressed in the protocol.

Comment 25

Please include all the Figure Legends together at the end of the Representative Results in the manuscript text. Each Figure Legend should include a title and a short description of the data presented in the Figure and relevant symbols. The Discussion of the Figures should be placed in the Representative Results. Details of the methodology should not be in the Figure Legends, but rather the Protocol.

Response

The figure captions are placed after representative results section in the suggested format.

Comment 26

Please obtain explicit copyright permission to reuse any figures from a previous publication. Explicit permission can be expressed in the form of a letter from the editor or a link to the editorial policy that allows re-prints. Please upload this information as a .doc or .docx file to your Editorial Manager account. The Figure must be cited appropriately in the Figure Legend, i.e. "This figure has been modified from [citation]."

Response

The copyright permissions are obtained and are submitted along with the revision. All the relevant figures and text has been cited appropriately.

Comment 27

As we are a methods journal, please revise the Discussion to explicitly cover the following in detail in 3-6 paragraphs with citations:

a) Critical steps within the protocol

b) Any modifications and troubleshooting of the technique

c) Any limitations of the technique

d) The significance with respect to existing methods

e) Any future applications of the technique

Response

The discussion section has been updated to include all the above suggested points on lines 277–320.

Comment 28

We do not have a separate conclusion section. Please merge it with the discussion section instead.

Response

The conclusion section is removed and merged with discussion section.

Comment 29

Please remove the embedded figure(s) from the manuscript. All figures should be uploaded separately to your Editorial Manager account. Each figure must be accompanied by a title and a description after the Representative Results of the manuscript text. All panels of one figure should be combined. Please do not put the legends along with the figures.

Response

A separate file for figures is created, captions are updated to have a title and short description. The revised manuscript is updated as per the above instructions.

Comment 30

Please revise the table of the essential supplies, reagents, and equipment. The table should include the name, company, and catalog number of all relevant materials in separate columns in an xls/xlsx file.

Response

The table of the essential supplies, reagents, and equipment is revised as per the instructions.

Reviewer 1

Comment 1

In Fig1a step 4, the top Ti and Pt has a larger lateral area than VOx, while in Fig. 1b they are of the same size. The authors need to make them consistent.

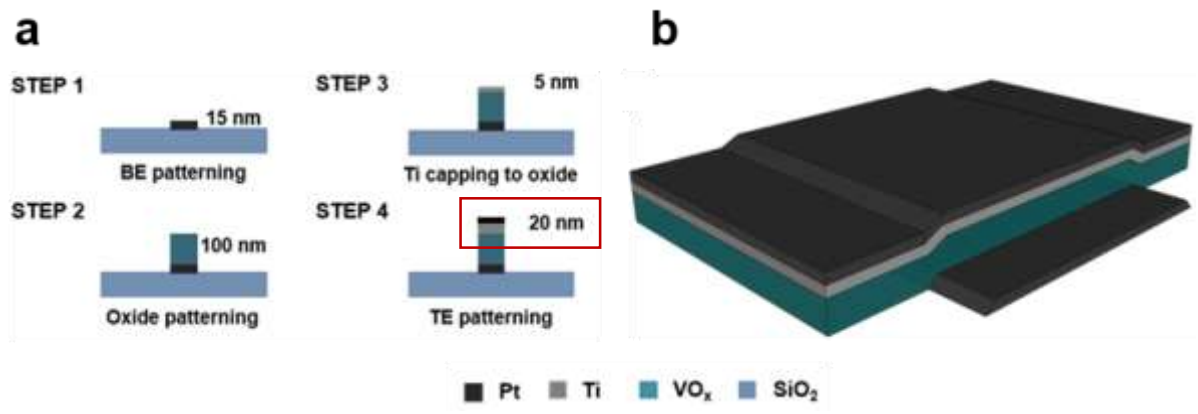
Response

We thank the Reviewer for bring it to our attention. The fabrication flow Fig 1a has been modified to match the device schematic

Modification

In Figures document

Modified section in highlighted in red boundary.



Comment 2

The lateral size of the defined cross bar was not discussed in the manuscript.

Response

We thanks the Reviewer for bringing this to our attention. The device dimensions are included in the manuscript.

Modification

Page 7, Line 286

Devices are fabricated with two different sizes for electrical testing, 4 x 4 µm and 6 x 6 µm.

Comment 3

The annealing conditions were not mentioned in the paper, which is important to avoid the degradation of the electrode.

Response

We are aware that annealing is used to condition the electrode metals and understand the Reviewer's concern here. However, our films are deposited using electron beam evaporation and they have been tested to render really good conductivity. Additionally, the electrode material used here is platinum (Pt) with adhesion of titanium (Ti). Pt being noble metal degradation is minimal.

From device structure point of view, the aim here was to study amorphous vanadium oxide as functional oxide in a sandwiched metal-oxide-metal or cross-point structure. Annealing would render uniform crystalline vanadium oxide. We have tested that for crystalline vanadium oxide top electrode and bottom electrode gets short due to very porous nature of our crystalline vanadium oxide film due to pinholes and grain boundaries.

Considering the above two points electrode annealing was not used in this case. As it is an important point, the explanation regarding this is added in the revision manuscript in discussion section.

Modification

Page 7 Lines 287-289

The contact electrode used here is Pt, which being a noble metal has minimal degradation over the period. Due to this and to avoid the uniform crystallisation of vanadium oxide in device structure, the normally used electrode annealing step was omitted in our fabrication.

Comment 4

I suggest the authors add the following references to further motivate their study, because such a technique is generally useful for crossbar devices and not limited to VOx: Proceedings of the IEEE 103, 1289 (2015).

Response

We thank the Reviewer for referring us to the above study. The above reference is included in the introduction section.

Modification

Page 10, Line 345

3 Zhou, Y. & Ramanathan, S. Mott Memory and Neuromorphic Devices. *Proceedings of the IEEE.* **103** (8), 1289-1310, (2015).

Page 2, Line 56-57

Multiple switching behaviours have been proposed for resistive switching devices till date.[2,3]

Reviewer 2

Major Concerns:

There are major gaps in the procedures (or in the explanation of the procedures) required to arrive at the conclusions stated in this manuscript. Some of these are concerns with the conclusions drawn in their previously published manuscript (Ref. [3] in Adv. Elec. Mat.). Although this is not a review of a previously published work, this is a criticism of the conclusions stated or referenced in this manuscript as having been drawn from the experimental process followed in this manuscript. I will stick to criticizing the procedures and their rigor, and not the scientific merits of the results. Below I list a few:

Comment 1

The presence of crystalline islands in an amorphous film need not have anything to do with the mechanism of volatile threshold switching. IMT can happen in either amorphous or crystalline films. Moreover, an amorphous film typically has short-range ordering that is not detected by spectroscopic techniques. So you have not used this set of experiments to explain this aspect. While this claim is in your previously published paper, I believe it is a far stretch and should not be claimed here.

Response

First of all we thanks the Reviewer for his time for critical consideration of both this paper and our previously published manuscript.

IMT happens only in the crystalline VO_2 and not in the amorphous VO_2. We have presented the proofs regarding this in our previous publication – Supporting information Figure S2 of the cited reference.[3] Additionally, it is also supported in the literature.[4-6]

About the second point regarding spectroscopic techniques, the focus of this study is to explain the experimental methodology of device fabrication, lamella preparation, and *in situ* biasing in TEM chamber. The representative results uses high resolution TEM micrographs and the corresponding diffraction patterns. While it is very much possible to do the spectroscopic analysis *in situ* using electron energy loss spectroscopy (EELS) in TEM chamber, it was not used this time.

We certainly agree with the Reviewer that the detailed explanation of the previously published results is beyond the scope of this paper. We have removed the detailed explanation in this paper and replaced it with the short summary in the representative results section as presented below.

Modification

Page 6, Lines 201-204

Note: *Once the aforementioned setup is ready data relating to TEM imaging, diffraction patterns, electron diffraction X-ray spectroscopy (EDX), and electron energy loss spectroscopy (EELS) mapping can be collected at different biasing voltages in situ. The representative results are presented in the later section.*

Page 7, Lines 228-231

The strong evidence for the presence of *c*-VO_2 islands in *a*-VO_x devices after biasing at higher voltage helped to prove the resistive switching characteristics (Figure 2 of cited reference[7]) and the switching mechanism (Figure 6 of the cited reference[7]) for asymmetric cross-point devices based on mixed-phased *a*-VO_x.

Comment 2

Are your TEM maps obtained while holding a current or voltage? I would guess not (from the text), but it is not clear. If the TEM maps are not obtained when holding a current/voltage, then it is misleading to call it an in-situ technique.

Response

Yes, Reviewer understanding here is correct. The TEM micrographs are not obtained while holding the constant voltage bias. They are obtained in remanence, immediately after the voltage sweep has finished. For clear and high quality TEM micrographs a focus adjustment is always required just before capturing the image which takes some time. The voltage sweeps are quick and there is no sufficient time to capture a high quality micrograph during the bias.

For the scope of this protocol, it is very much possible to hold the constant voltage bias instead of voltage sweeps and capture TEM micrographs while holding the constant voltage bias, which will be truly an *in situ* as Reviewer is suggesting. Even in that case the complete protocol – the process of device fabrication, lamella preparation, and *in situ* TEM will remain exactly the same from methodology point of view. Just instead on voltage sweeps, we will apply constant voltage which is a tiny modification on the software controlling source-meter.

Even in the constant voltage bias mode there is a tread-off. The energy applied to the sub-100 nm thin lamella with constant voltage will be different at different intervals of time. Due to this the nanostructural changes captured at different time intervals can possibly be different.

In our previously published results experimental requirements were of voltage sweeps. For those results, we do partially agree with the Reviewer. However, there are two points we would like to mention. One, we only report of *in situ* TEM micrographs and not any compositional changes which can be possibly different during the voltage sweeps and immediately after the sweep. Second, the formation of *c*-VO_2 islands as a results of voltage sweeps was observed manually to happen during the bias and it being an irreversible change remained the same even after the voltage sweep was finished. Considering these points, the data collected in remanence in this case should be acceptable as *in situ*.

We believe both constant voltage and voltage sweeps have tread offs which are insignificant. For the scope of the protocol explained here, the methodology remains the same regardless of constant voltage or voltage sweep mode.

Modification

Page 7, Line 233

The results show the application of the explained protocol. Here the *in situ* nanostructural changes are captured in remanence of voltage sweeps at different voltages with the high resolution TEM (HRTEM) micrographs and corresponding diffraction patterns.

Page 6, Line 204

Note: *Once the aforementioned setup is ready data relating to TEM imaging, diffraction patterns, electron diffraction X-ray spectroscopy (EDX), and electron energy loss spectroscopy (EELS) mapping can be collected at different biasing voltages in situ by applying either constant voltage or voltage sweeps with the control PC and source meter software as explained in fabrication process and electrical characterisation section.*

Comment 3

Crystal islands do not explain two-step switching. You should have held the voltage at intermediate levels between two switching events to see if indeed only a part of the crystal islands switched. I don't think this was done, and is a major gap in the procedure used to draw the conclusions you have.

Response

We thanks the Reviewer for this point. The experiment he is suggesting was already performed and presented in our previous publication (Figure 2f and inset) electrically.[8] The role of *in situ* TEM results in the mechanism of two-step switching was limited to observing multiple nucleation sites and crystal islands orientated in different directions with respect to the substrate as a result of biasing, which it clearly shows in Figure 7. The complete conclusion in the previous publication was not based on just *in situ* TEM, but it was a combined conclusion of electrical characterisations, *in situ* TEM results, and a support literature where different crystal orientations of VO_2 have been reported to have different IMT temperatures. When the stimulus is voltage instead of temperature, different orientations of VO_2 crystal islands would switch at different voltages.

We believe this point was mainly the part of our previous publication and for the scope of this paper it is not very related. After careful consideration and to avoid confusions, we have removed this discussion from the representative results section and replaced it with a short summary.

Modification

Page 7, Lines 228-231

The strong evidence for the presence of *c*-VO_2 islands in *a*-VO_x devices after biasing at higher voltage helped to prove the resistive switching characteristics (Figure 2 of cited reference[7]) and the switching mechanism (Figure 6 of the cited reference[7]) for asymmetric cross-point devices based on mixed-phased *a*-VO_x.

Minor Concerns:

The English usage in the manuscript can be improved. And there are a few mistakes (for instance, you wrote "nucleation sights" instead of "nucleation sites", also found in the earlier published paper).

Response

We thank the reviewer for bringing it to our attention. The spelling typos have been carefully checked and corrected throughout the revised manuscript.

Another minor concern is self-plagiarism. Some of the figure panels, and in some cases entire figures have been reproduced from your earlier published paper. And so are some parts of the text. Please revise all the text, and I suggest change the figures in some minor ways (orientation, ordering, coloring, etc.) or you will have to obtain permission to reuse the figures. The Editor should be able to assist you here.

Response

We again thanks the Reviewer for their careful observations. This point has been discussed with the Editor and the copyright permissions are submitted. Figures and text have been cited appropriately where required to address the self-plagiarism issue.

References

[1] F. Pan, S. Gao, C. Chen, C. Song, F. Zeng, *Materials Science and Engineering: R: Reports* **2014**, *83*, 1.

[2] Y. Zhou, S. Ramanathan, *Proceedings of the IEEE* **2015**, *103*, 1289.

[3] R. K. Yafarov, *Semiconductors* **2018**, *52*, 137.

[4] J. A. Rupp, M. Querré, A. Kindsmüller, M.-P. Besland, E. Janod, R. Dittmann, R. Waser, D. J. Wouters, *Journal of Applied Physics* **2018**, *123*, 044502.

[5] J. Rupp, R. Waser, D. Wouters, "Threshold Switching in Amorphous Cr-doped Vanadium Oxide for New Crossbar Selector", presented at *Memory Workshop (IMW), 2016 IEEE 8th International*, **2016**.

[6] M. Taha, S. Walia, T. Ahmed, D. Headland, W. Withayachumnankul, S. Sriram, M. Bhaskaran, *Scientific Reports* **2017**, *7*, 17899.

[7] S. Nirantar, E. Mayes, M. A. Rahman, T. Ahmed, M. Taha, M. Bhaskaran, S. Walia, S. Sriram, *Advanced Electronic Materials* **2019**, 1900605.

[8] S. Nirantar, E. Mayes, M. A. Rahman, T. Ahmed, M. Taha, M. Bhaskaran, S. Walia, S. Sriram, *Advanced Electronic Materials* **2019**, *0*, 1900605.