

Supporting Information

The formation of TiO₂/VO₂ multilayer structure via directional cationic diffusion

Yonghui Zheng¹, Zhuo Chen¹, Hao Lu², Yan Cheng^{3,4}, Xin Chen⁴, Yunbin He², Zaoli Zhang¹

¹*Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, A-8700 Leoben, Austria*

²*Ministry of Education Key Laboratory of Green Preparation and Application for Functional Materials, Hubei Key Lab of Ferro & Piezoelectric Materials and Devices, Hubei Key Laboratory of Polymer Materials, School of Materials Science and Engineering, Hubei University, Wuhan 430062, China*

³*Key Laboratory of Polar Materials and Devices (MOE), Department of Electronics, East China Normal University, Shanghai 200241, China.*

⁴*State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China.*

Corresponding authors:

ycheng@ee.ecnu.edu.cn; ybhe@hubu.edu.cn; zaoli.zhang@oeaw.ac.at

Fig. S1. Top-view SEM images and corresponding elemental distribution for (a-d) U-VO₂ and (e-h) A-VO₂.

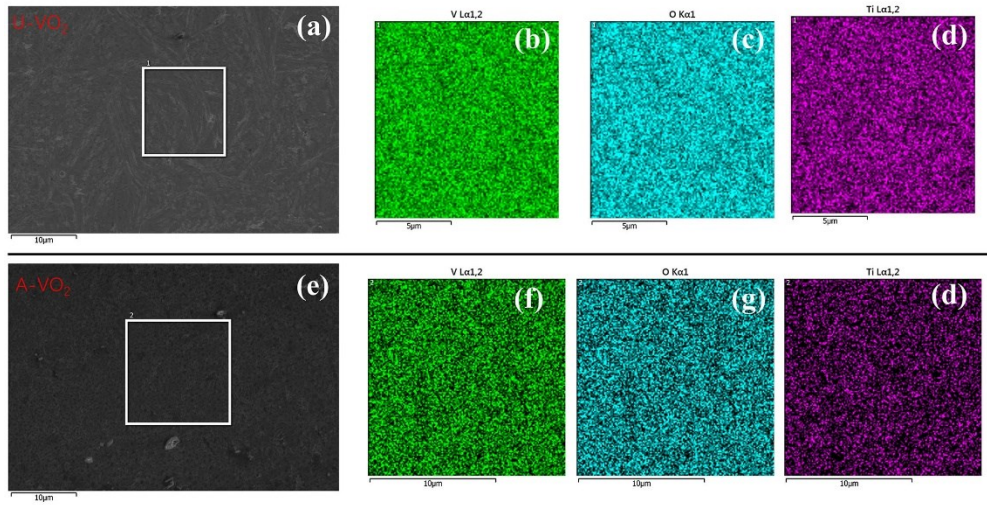


Fig. S2. Elemental distribution when the film is annealing in a shorter time (5 min at 500 °C). At this time, Ti-rich nano-lamellas perpendicular to c axis of R-phase are also observed. However, the width is narrower than that with a longer annealing time.

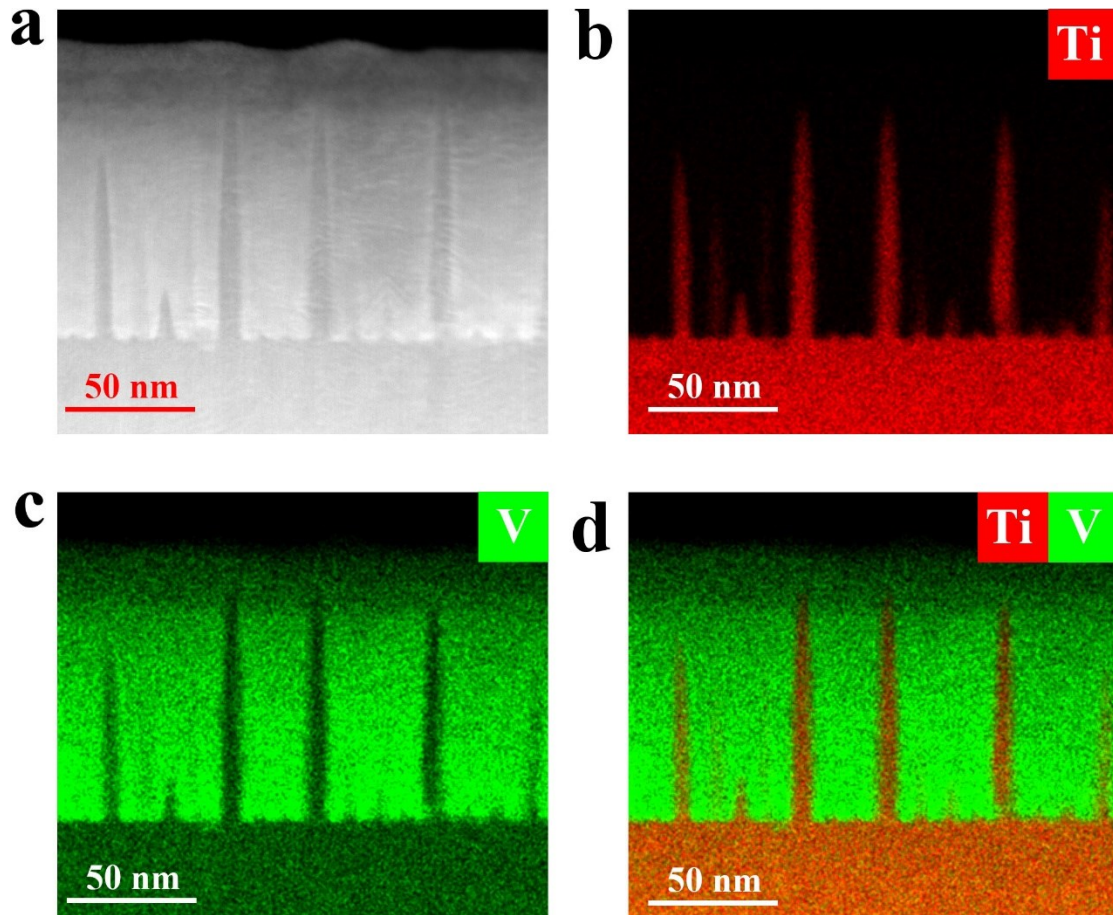
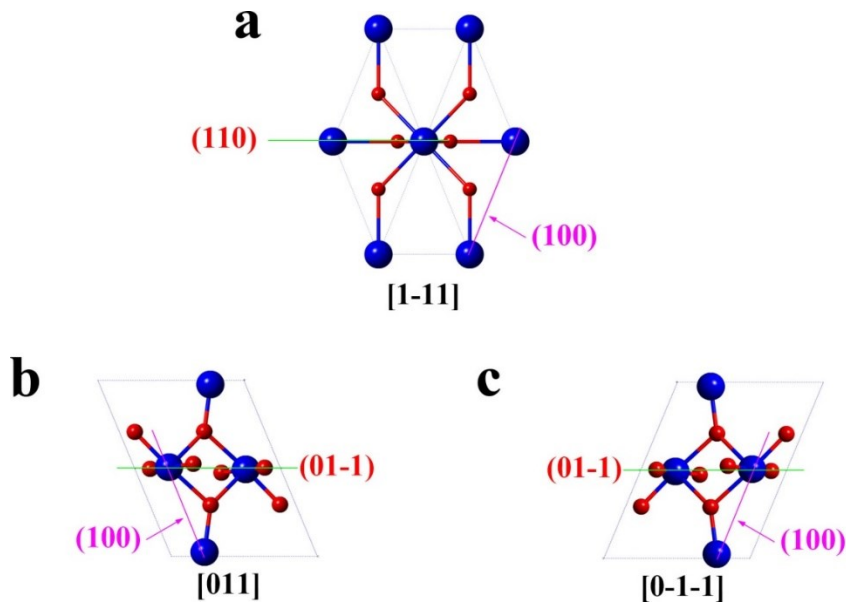


Fig. S3. (a) Atomic structure of R-phase (upper area) and (b-c) M-phase (lower area) VO₂. A mirror symmetry between (b) and (c) can be found, with a slightly atomic movement, both would transform into R-phase with the same direction, that is [111] orientation of R-phase. (d) The overlay of typical diffraction patterns of M-phase projected along [011]_M and [0 $\bar{1}\bar{1}$]_M directions, in which the left half is from the experimental result, and the right half is from the simulated one. (e) The diffraction patterns of R-phase projected along [111] direction (corresponding the [011]_M or [0 $\bar{1}\bar{1}$]_M direction in M-phase), in which the left half is from the experimental result, and the right half is from the simulated one. Comparing the difference of the diffraction patterns, we can alternatively select the additional spots in M-phase diffraction patterns to depict the detailed distribution of M-phase domains through DF images.



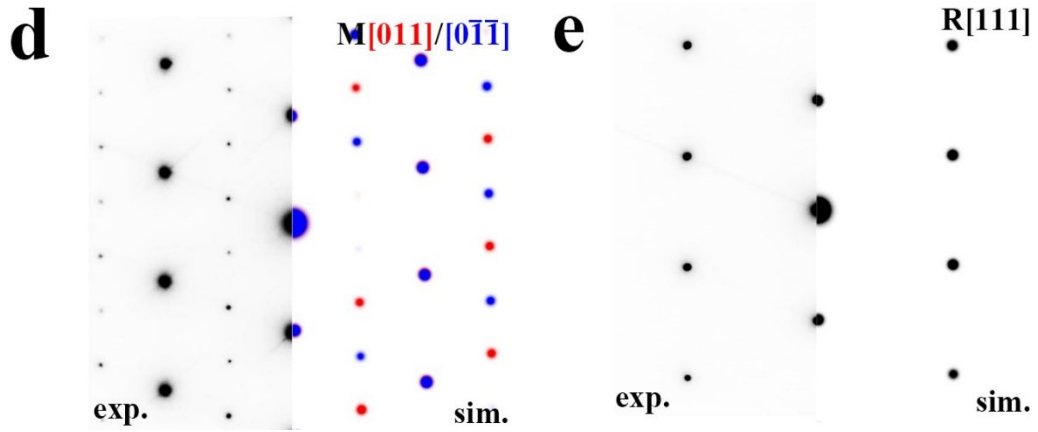


Fig. S4. (a) BF image of A-VO₂ film viewed from [110] direction. (b) BF image of A-VO₂ film viewed from [111] direction. Due to the anisotropic strain field, a gradually reduced dark contrast starting from the nano-lamella boundary can be found when viewed from [110] direction. When tilting to [111] direction, it shows a dark contrast inside the nano-lamella.

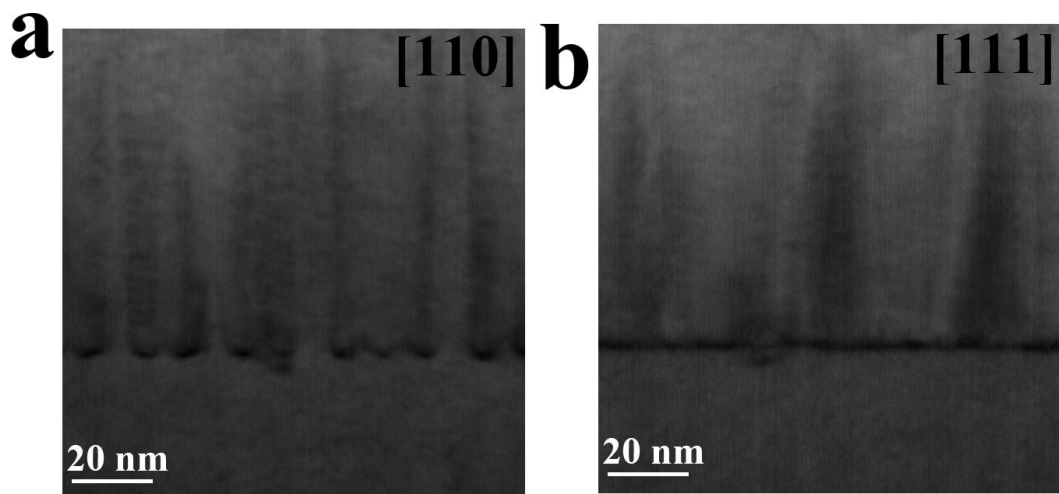


Fig. S5. (a) HAADF, (b) LAADF and (c) BF images in A-VO₂ film. In which the LAADF image shows an extremely bright contrast, BF shows a complementary dark contrast and HAADF image shows a reduced bright diffuse contrast around the strain lines area.

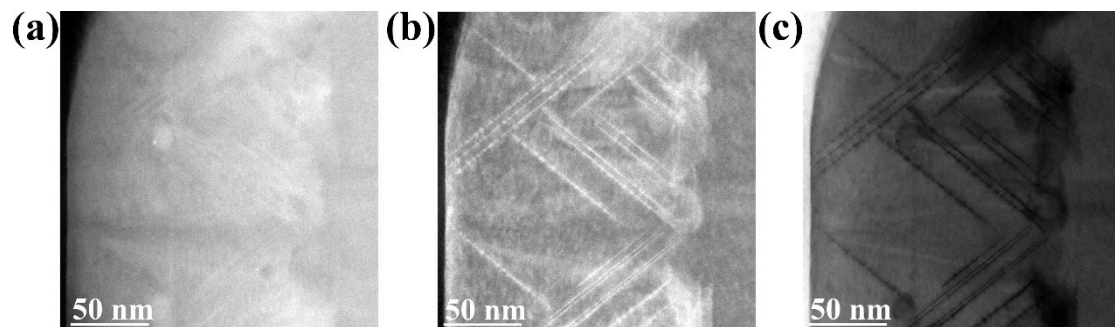


Fig. S6. (a) Initial parallel strain lines (denoted by the red circle) inside A-VO₂ film at room temperature. (b) Heating up to 90 °C to transform the film to R-phase. (c) After heating, the sample is cooled to room temperature and recovered to M-phase. During the whole operating process, the strain lines don't change and disappear. Therefore, these strain lines are very stable, and the formation of these strain lines should be related to the initial thermal treatment at elevated temperatures.

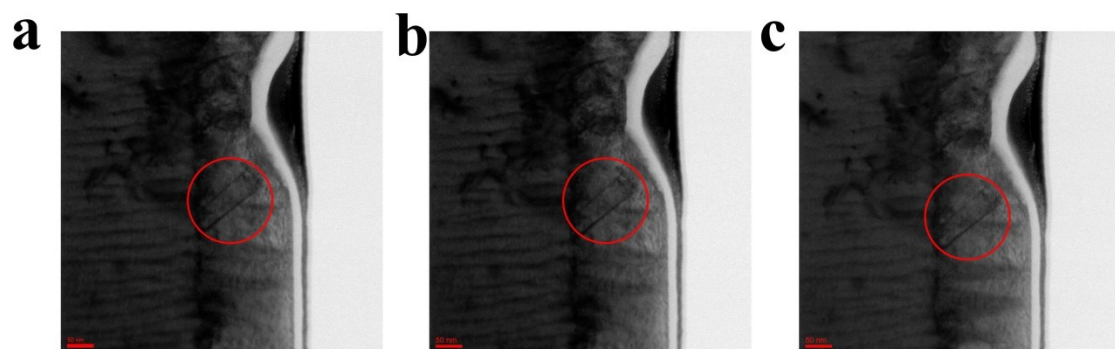


Fig. S7. (a) LAADF morphology viewed from $[110]$ orientation. (b) LAADF morphology viewed from $[111]$ orientation. Two extremely bright strain lines are denoted by red arrows). Besides, they are much sharper when viewed from $[111]$ direction than $[110]$ orientation.

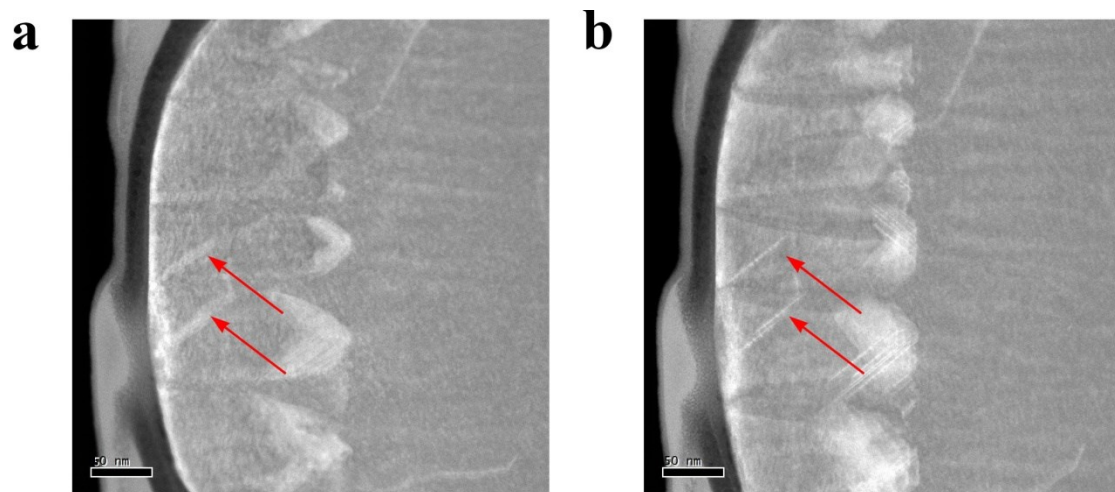


Fig. S8. The reversible phase transition in U-VO₂ films. *In situ* heating/cooling microstructure evolution at different temperature (a-h) in U-VO₂ films. It's found that M-phase domains remain stable at 65 °C during the heating process, and start to evolve into R-phase (dark contrast) at 80 °C. The whole film completely transforms into R-phase with a homogenous dark contrast at 85 °C. As for the cooling process, some R-phase domains at the interface area recover to M-phase at 70 °C, and returns to initial M-phase at 60 °C.

