

Article

Metastability Phenomena in VO₂ Thin Films

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Abstract: VO₂ is a transition metal oxide in which complex electronic phases appear near the metal-to-insulator transition due to electron correlation and electron–lattice interactions. This system is characterized by a metal-to-insulator transition (MIT) at around 341 K. The metal (high T) phase is tetragonal while the insulator (low T) phase is monoclinic and the resistivity changes at the MIT by about five orders of magnitude. Here, we report investigations of the MIT in a thin VO₂ film deposited on a sapphire substrate showing hysteresis. The MIT has been characterized by resistance measurements versus temperature and a DC magnetic field. The thin sample shows different final resistance values in both the insulating and metallic state after different temperature cycles. Moreover, some cycles do not close in the insulating phase. An unexpected magnetic dependence of the temperature cycle in the sample was also observed. The results show that the MIT of VO₂ can be controlled by reducing the thickness below 40 nm in micron-sized ribbons since MIT is associated with the emergence of coexisting metastable conformations controlled by the thickness-dependent misfit strain and stress distributions induced by the mismatch between thin ribbon film and the substrate.

Keywords: VO₂ oxide; strain in thin layer and interface; metal–semiconductor interfaces

1. Introduction

Vanadium dioxide (VO₂) is a transition metal oxide which exhibits unique complex phases where both electronic correlation, local lattice fluctuations, orbital ordering and charge ordering play a key role. These competing interactions are at the origin of the complex electronic and structural metal-to-insulator transition (MIT) observed around 341 K [1–3]. The MIT in VO₂ is highly sensitive to chemical and physical local perturbations, e.g., strain/stress [1,4,5] affects the temperature transition and the final resistance in the insulating phase is affected by the distribution of the M1 and M2 phases where the latter is three times more resistive than M1. The metallic and insulating phases and the transition changes across the MIT in VO₂ thin films, are controlled by the electronic orbital occupation tuned by the local strain [3]. This effect has been confirmed and further demonstrated to be reversible by the incorporation of hydrogen into VO₂ thin films [6]. The hysteresis cycle indicates the emergence of an arrested nanoscale phase separation during the transition, and structural defects

and the quenched disorder at nano/micro-scale contribute to a complex landscape with multiple domains where different phases coexist [4]. For a single domain, the hysteretic cycle temperature width, ΔT , is around 5 K [4], while in multi-domains the temperature width, ΔT , of the phase transition increases [7]. The low dimensionality of the film structure and the lattice mismatch (misfit) with the substrate contribute to a nanoscale inhomogeneity. The aim of this work is to investigate this complex scenario in VO₂ thin films since the control of the quenched disorder superstructures at the nanoscale is technologically important to make VO₂ a functional material [8,9]. Indeed, we will show that low dimensionality VO₂ thin films show a non-conventional resistance behavior with metastable resistance states in both the insulating and the metallic phase. Moreover, some cycles show an initial insulating resistive state that is different from the final one, i.e., the hysteresis loop remains open. This condition points out the coexistence of two insulating phases: M1 and M2, where M2 is about three times more resistive than M1, or the presence of metal domains embedded in the insulating matrix [10,11]. Finally, in the thin VO₂ sample, by increasing the magnetic field, the temperature loop width ($\Delta T(K)$) increases, in clear disagreement with the well-known independent behavior from the magnetic field of the bulk VO₂ [12].

2. Results

We report low dimensionality effects on the MIT of a VO₂ thin ribbon film of $d_a = 40$ nm height, of width $W_a = 514 \mu\text{m}$ and length $L_a = 4541 \mu\text{m}$. The thin film is sensitive to the substrate surface microstructure and misfit strain. We have measured the resistance as a function of temperature and high magnetic field, of the VO₂ thin film. The characteristics of this sample are representative of a series of thin films realized with different thickness and width, which exhibited similar hysteresis cycles. In Figure 1a, we compare the hysteretic resistance cycles for different magnetic field amplitudes. The resistance values depend on both the time evolution during the cycle, called τ_c , and the “waiting time” among cycles, called τ_w .

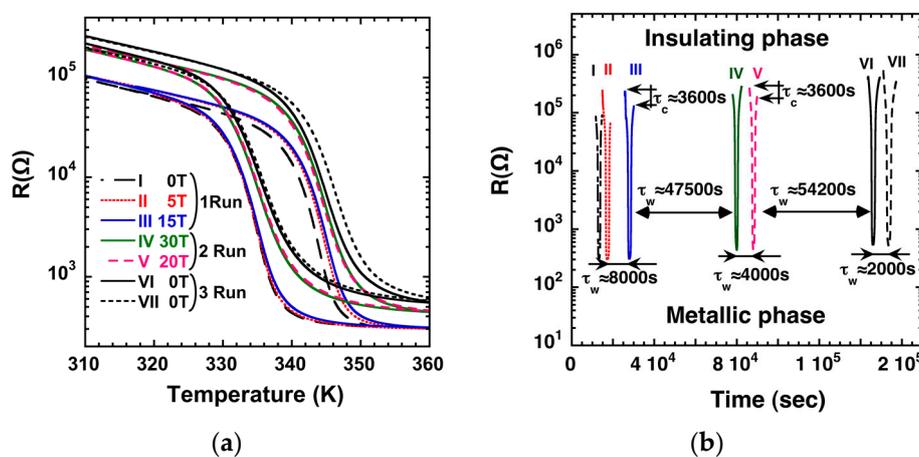


Figure 1. (a) Hysteretic resistance cycles of a VO₂ film with thickness $d = 40$ nm and width $W = 514 \mu\text{m}$ measured in the range 290–370 K and 0–30 T. 1 run: I (0 T), II (5 T), III (15 T); 2 run: IV (30 T), V (20 T); 3 run: VI (0 T), VII (0 T). (b) The time evolution of the resistance cycles (more details in the text).

The sample shows the MIT transition while heating at around 340 K, and in the cooling procedure at ~ 330 K. These values have been calculated from the peaks of the plots of $dR(\Omega)/dT$ versus T. The VO₂ sample exhibits, in the same run, small differences in the resistance values in the final insulating and metallic states after temperature cycles, while differences increase among different runs (Figure 1a,b). These effects can be explained considering the waiting time (τ_w) among runs, which is longer by about one order of magnitude compared to τ_c in the same run. In this context, the electrical resistance values are dominated by the comparison between the experimental time to measure the hysteresis cycles

(τ_c) and the waiting time (τ_w) between two hysteresis cycles. The latter have to be compared with the characteristic times of formation of the insulating and metallic phase in the VO₂ sample, called τ_i and τ_m . In particular, these characteristic times (τ_i , τ_m) depend on the structure of the material at the nanoscale, since local stress/strain may increase these characteristic times. Actually, if τ_c and τ_w are shorter than τ_i and τ_m , then the VO₂ system may reach metastable states which will evolve over time. In this framework, open cycles in the insulating phase can be observed (Figure 2). This behavior underlines history dependence.

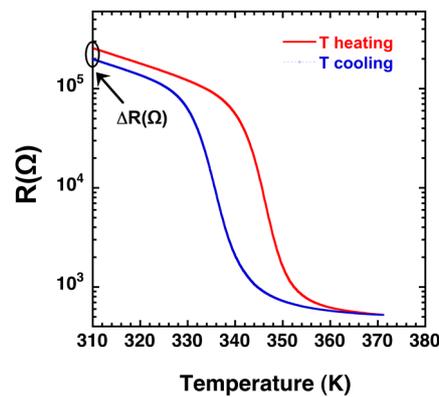


Figure 2. An example of a hysteresis loop that is not closed in the insulating state.

Regarding the application of high magnetic fields, the VO₂ resistance shows an “unexpected weak magnetic dependence” that points out a different behavior with respect to the well-recognized invariance of the resistance versus the magnetic field observed in bulk VO₂ samples [10]. To clarify this issue, we show the temperature variation ($\Delta T(K)$) of the hysteresis loop width as a function of the magnetic field. We analyzed the behavior of the derivative of the resistance $dR(\Omega)/dT(K)$.

In Figure 3a, we show the behaviors for two magnetic fields: 0 T and 30 T. The comparison highlights changes in the shape of the hysteresis cycle, possibly related to the structure of the VO₂ film and, in particular, to internal stresses at the nanoscale. In Figure 3b, we show the dependence of $\Delta T(K)$ as a function of the magnetic field.

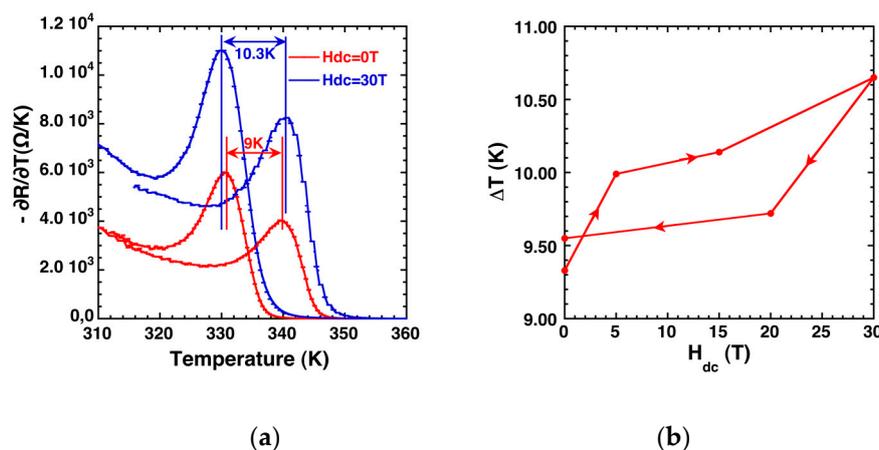


Figure 3. (a) Hysteretic derivative resistance cycles in the range 290 K–370 K at 0 T and 30 T. (b) The hysteresis loop temperature width versus H_{dc} (T).

Samples showing the occurrence of open cycles or different values of the resistance in the two phases while a high magnetic field and the temperature are changed, show “metastable” conformations that depend on the time history and on the local structure of the sample. At first approximation, they

are not affected by the presence of the strong magnetic field. Actually, we may claim that the magnetic field alone is not sufficient to induce metastable conformations in thin films of VO₂.

3. Discussion

The resistance measurements, as a function of the temperatures for the VO₂ film, show the presence of metastable final states (Figures 1 and 2). This *metastability* is present for both insulating and metallic states. Moreover, some resistance measurements have shown that the initial insulating metastable phase has a different value with respect to the final value in the same resistive hysteresis loop. These observations, together with a broad MIT transition, indicate the co-existence of multi-domains that nucleate and grow and/or shrink during the transition. These domain patterns are formed spontaneously and result from the competition between the strain/stress *misfit energy* in the VO₂ film and the substrate, together with the *wall energy* of the same domains [4]. The metastable state resistance is also associated with the time and thermal history of the VO₂ film (Figures 1 and 2). In fact, there is also an interplay between the *characteristic time scale*, τ_I and τ_M associated to the insulating and the metallic phase; and the *changing time* of the measure, such as the experimental time to measure the hysteresis cycle, τ_c , and the waiting time, τ_w , between two hysteresis cycles [13]. In this framework, the *metastability* during the MIT in VO₂ is driven by defects, non-homogeneities, quenched disorder and symmetries at the nano/micrometer-scale, influenced by local stress/strain due to the misfit between the film and the substrate. This aspect is present not only in VO₂, but in all “transition metal oxide” materials, such as high temperature superconductor (HTSC) materials (HTSC), for which the critical temperature and the “magnetic flux pinning” depend on the self-assembling of the quenched disorder in the structure [8,9]. The *metastability* in this VO₂ thin film is assigned to the competition between the two insulating phases (M1 and M2) with different resistance values [4] and/or the possible presence of persistent metallic domains in the final insulating phase [10]. Surprisingly, the dependence on the magnetic field is also observed in other similar low-dimensional systems such as self-assembly VO_x nanotubes [14] or in defective VO₂ thin films [15]. This is an indication that in the VO₂ sample, the magnetic field modulates the formation of multi-domains that in turn regulate the gradual variation of the phase during the MIT transition in a wide range of temperatures [1].

4. Materials and Methods

The VO₂ film was prepared at the University of Science and Technology of China (Hefei, China). In particular, VO₂ films were realized on Al₂O₃ (0006) single crystal substrates by a RF-plasma assisted oxide Molecular Beam Epitaxy (MBE) instrument (assembled in house for oxide materials growth, at University of Science and Technology of China, Hefei, China) with a base pressure better than 3×10^{-7} Pa. Prior to the VO₂ deposition, the Al₂O₃ (0001) substrates were ultrasonically cleaned in sequence: acetone, isopropanol and deionized water, for 10 min each. After this treatment, the substrate was blown dry by N₂ flux and then rapidly transferred inside the vacuum chamber. During the deposition, the substrate temperature was kept at 530 °C and the oxygen flux was kept at 3.6 sccm. After, Au stripes were realized on the as-grown VO₂ films following this procedure: the poly(methyl methacrylate) (PMMA ~1 μm thick) was first coated by spin-coating and then exposed, with an optical mask, to ultraviolet (UV) light (365 nm). After chemical removal of the exposed PMMA, ~50 nm Au was deposited by electron-beam evaporation. Finally, 5 mm-length Au stripes with 100 μm and 500 μm width were obtained by removal of the extra PMMA. For the electrical transport measurement, Au stripes were connected to the external electrical circuit with Al wires of 25 μm by a wire bonding instrument (West Bond, 747677E, West-Bond, Anaheim, CA USA).

The resistance measurements at high magnetic field have been performed at the “High Field Magnet Laboratory” Institute for Molecular and Material of the Radboud University (Nijmegen, The Netherlands). For the measurements, we used a cryostat with an external normal magnet and a chip carrier with the VO₂ sample has been mounted on the cryogenic insert. The temperature cycles were controlled using the LakeShore 340 Cryogenic Temperature Controller (Lake Shore Cryotronics Inc.,

Westerville, OH, USA) and the temperature was measured by a cernox thermometer glued on the sample-holder. For resistance measurements, voltage and current have been measured using the Keithley Source Meter 2611 (Keithley, Solon, OH, USA). The temperature range and temperature sweep rate are $290\text{ K} < T < 370\text{ K}$ and $R = 2\text{ K/min}$, respectively, while the DC magnetic field range is $0\text{ T} < H_{\text{dc}} < 30\text{ T}$.

5. Conclusions

This work reports the resistivity properties of a VO_2 thin low dimensional film. The misfit between substrate/film, regulated by defects and quenched disorder, gives important contributions that dominate the MIT resistive response. By controlling the thickness and width of thin films, it is possible to change the resistive response. This sample shows a clear *metastability* of the final resistivity value in the insulating/metallic phase after hysteresis temperature cycles. The emerging nanoscale inhomogeneity in the vanadium dioxide at the metal-to-insulator transition is well known and makes this system similar to other complex high correlated quantum materials [8,9,16–20] where the phase separation landscape depends on misfit strain [16,17]. We show that by reducing the thickness below 40 nm in micron-sized ribbons, we can control the complex nano-phase separation at MIT of VO_2 . Moreover, the VO_2 thin film ribbon shows an “unexpected high magnetic field dependence” that points out the possibility to tune magnetic ordering by controlling the multi-domain dynamics of the vanadium oxide. This behavior indicates the presence of *metal localized states* or a combination of “different $M1, M2$ insulating local phases” that affect the final insulating/metallic states. It appears evident that the possibility to control misfit, inhomogeneity and defects at the nanoscale near the metal-to-insulator transitions opens the opportunity to functionalize the VO_2 at low dimensionality and to design unique nanoscale devices.

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Author Contributions: Daniele Di Gioacchino, Augusto Marcelli and Antonio Bianconi conceived and designed the experiments; Daniele Di Gioacchino, Augusto Marcelli, Alessandro Puri, Uli Zeitler performed the experiments; Daniele Di Gioacchino, Alessandro Puri, Augusto Marcelli analyzed the data; Chongwen Zou, Lele Fan contributed to realized films and analysis tools; Daniele Di Gioacchino, Augusto Marcelli wrote the paper. All authors have read and approved the final manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Pouget, J.; Launois, H.; Haenens, J.P.; Merenda, P.; Rice, T.M. Electron Localization Induced by Uniaxial Stress in Pure VO_2 . *Phys. Rev. Lett.* **1975**, *35*, 873–875. [[CrossRef](#)]
2. Bianconi, A. Multiplet splitting of final-state configurations in x-ray-absorption spectrum of metal VO_2 : Effect of core-hole-screening, electron correlation, and metal-insulator transition. *Phys. Rev. B* **1982**, *26*, 2741–2747. [[CrossRef](#)]
3. Aetukur, N.B.; Gray, A.X.; Drouard, M.; Cossale, M.; Gao, L.; Reid, A.H.; Kukreja, R.; Ohldag, H.; Jenkins, C.A.; Arenholz, E.; et al. Control of the metal-insulator transition in vanadium dioxide by modifying orbital occupancy. *Nat. Phys.* **2013**, *9*, 661–666. [[CrossRef](#)]
4. Cao, J.; Wu, J. Strain effect in low-dimensional transition metal oxides. *Mater. Sci. Eng.* **2011**, *R71*, 35–52. [[CrossRef](#)]
5. Nakano, N.; Shybaya, S.; Okuyama, D.; Hatano, T.; Ono, S.; Kawasaki, M.; Iwasa, Y.; Tokura, Y. Collective bulk carrier delocalization driven by electrostatic surface charge accumulation. *Nature* **2012**, *487*, 459–462. [[CrossRef](#)] [[PubMed](#)]
6. Yoon, H.; Choi, M.; Lim, T.; Kwon, H.; Ihm, K.; Kim, J.K.; Choi, S.; Son, J. Reversible phase modulation and hydrogen storage in multivalent VO_2 epitaxial thin films. *Nat. Mater.* **2016**, *15*, 1113–1119. [[CrossRef](#)] [[PubMed](#)]

7. Cao, J.; Ertekin, E.; Srivasan, V.; Fan, W.; Huang, S.; Zheng, H.; Yim, J.W.L.; Khanal, D.R.; Ogletree, D.F.; Grosman, J.C.; et al. Strain engineering and one-dimensional organization of metal–insulator domains in single-crystal vanadium dioxide beams. *Nat. Nanotechnol.* **2009**, *4*, 732–737. [[CrossRef](#)] [[PubMed](#)]
8. Poccia, N.; Ricci, A.; Campi, G.; Fratini, M.; Puri, A.; Di Gioacchino, D.; Marcelli, A.; Reynolds, M.; Burghammer, M.; Saini, N.L.; et al. Optimum inhomogeneity of local lattice distortions in $\text{La}_2\text{CuO}_{4+y}$. *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 15685. [[CrossRef](#)] [[PubMed](#)]
9. Di Gioacchino, D.; Puri, A.; Marcelli, A.; Poccia, N.; Ricci, A.; Bianconi, A. The flux dynamics behavior of the two competing high temperature superconducting phases in underdoped $\text{LaCuO}_{4.06}$. *Phys. Chem. Chem. Phys.* **2016**, *18*, 12534. [[CrossRef](#)] [[PubMed](#)]
10. Ramírez, J.G.; Sharoni, A.; Dubi, Y.; Gómez, M.E.; Schuller, I.K. First-order reversal curve measurements of the metal-insulator transition in VO_2 : Signatures of persistent metallic domains. *Phys. Rev. B* **2009**, *79*, 235110. [[CrossRef](#)]
11. Wei, J.; Wang, Z.; Chen, W.; Cobden, D.H. New aspects of the metal–insulator transition in single-domain vanadium dioxide nanobeams. *Nat. Nanotechnol.* **2009**, *4*, 420–424. [[CrossRef](#)] [[PubMed](#)]
12. Berglund, C.N.; Guggenheim, H.J. Electronic Properties of VO_2 near the Semiconductor-Metal Transition. *Phys. Rev.* **1969**, *185*, 1022–1033. [[CrossRef](#)]
13. Agarwal, G.S.; Shenoy, S.R. Observability of hysteresis in first-order equilibrium and nonequilibrium phase transitions. *Phys. Rev. A* **1981**, *23*, 2719–2723. [[CrossRef](#)]
14. Krusin-Elbaum, L.; News, D.M.; Zeng, H.; Derycke, V.; Sun, J.Z.; Sandstrom, R. Room-temperature ferromagnetic nanotubes controlled by electron or hole doping. *Nature* **2004**, *431*, 672–676. [[CrossRef](#)] [[PubMed](#)]
15. Yan, T.H.; Nori, S.; Zhou, H.; Narayan, J. Defect-mediated room temperature ferromagnetism in vanadium dioxide thin films. *Appl. Phys. Lett.* **2009**, *95*, 102506.
16. Bianconi, A.; Di Castro, D.; Bianconi, G.; Pifferi, A.; Saini, N.L.; Chou, F.C.; Johnston, D.C.; Colapietro, M. Coexistence of stripes and superconductivity: T_c amplification in a superlattice of superconducting stripes. *Phys. C Supercond.* **2000**, *341–348*, 1719–1722. [[CrossRef](#)]
17. Di Castro, D.; Bianconi, G.; Colapietro, M.; Pifferi, A.; Saini, N.L.; Agrestini, S.; Bianconi, A. Evidence for the strain critical point in high T_c superconductors. *Eur. Phys. J. B Condens. Matter Complex Syst.* **2000**, *18*, 617–624. [[CrossRef](#)]
18. Dagotto, E. Complexity in strongly correlated electronic system. *Science* **2005**, *309*, 257–262. [[CrossRef](#)] [[PubMed](#)]
19. Campi, G.; Campi, G.; Bianconi, A.; Poccia, N.; Bianconi, G.; Barba, L.; Arrighetti, G.; Innocenti, D.; Karpinski, J.; Zhigadlo, N.D.; et al. Inhomogeneity of charge-density-wave order and quenched disorder in a high- T_c superconductor. *Nature* **2015**, *525*, 359–362. [[CrossRef](#)] [[PubMed](#)]
20. Marcelli, A. Phase Separations in Highly Correlated Materials. *Acta Phys. Polonica A* **2016**, *129*, 264–269. [[CrossRef](#)]

