



Review

Critical Review on the Phase Change Properties of VO₂: Influence of Synthesis Methods and Transition Mechanisms

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ABSTRACT

Vanadium dioxide (VO₂) is a strongly correlated material that exhibits a reversible metal-insulator transition (MIT) near room temperature (~68°C), accompanied by a structural phase transition from a monoclinic (M1, insulating) to a tetragonal rutile (R, metallic) phase. This unique property makes VO₂ a promising candidate for applications in smart windows, optoelectronic switches, and thermal sensors. However, the phase transition characteristics, such as transition temperature, hysteresis width, and optical/electrical contrast, are highly dependent on the synthesis method. This review critically examines the impact of different synthesis techniques (e.g., chemical vapour deposition, sol-gel, sputtering, pulsed laser deposition, and hydrothermal synthesis) on the phase transition properties of VO₂. A comparative analysis is presented, highlighting how stoichiometry, strain, defects, and doping influence the MIT. Additionally, the fundamental chemistry governing the phase transition is discussed, with a focus on electron correlation effects and lattice dynamics. A comprehensive comparison table summarises the synthesis methods, their effects on phase transition properties, and key challenges.

Keywords: Defect chemistry; Mott transition; Phase-change materials; Thermochromic materials

1. Introduction

Vanadium dioxide (VO₂) has emerged as one of the most intriguing functional materials in condensed matter physics and materials science due to its remarkable metal-insulator transition (MIT) near 68°C [1],[2]. This first-order phase transformation involves a reversible structural change from a low-temperature monoclinic phase (M1, P2₁/c space group) to a high-temperature tetragonal rutile phase (R), accompanied by dramatic alterations in its electronic and optical properties [3]. The transition manifests as an abrupt decrease in electrical resistivity by up to five orders of magnitude and significant modulation of infrared transmittance, making VO₂ particularly attractive for applications in smart windows, optical switches, and thermal sensors [4],[5]. These exceptional properties stem from the complex interplay between electron-electron correlations (Mott-Hubbard mechanism) and structural distortions (Peierls instability), positioning VO₂ as a prototypical system for

studying strongly correlated electron materials and coupled electronic-structural phase transitions [6],[7].

The physics underlying VO₂'s phase transition has been the subject of extensive research since its discovery in 1959 by Morin [8]. The insulating M1 phase features paired vanadium ions along the c-axis, creating a dimerised structure with split d|| orbitals that establish a bandgap of approximately 0.6 eV [1],[9],[10]. Upon heating through the transition temperature (T_i), these dimers dissociate, leading to a delocalisation of d-electrons and the formation of a metallic state with overlapping energy bands [11]. This electronic reorganisation occurs concomitantly with structural changes in the VO₆ octahedra coordination, where the V-V distance evolves from alternating short (2.65 Å) and long (3.12 Å) separations in the M1 phase to a uniform spacing (2.87 Å) in the R phase [5],[12]. The transition is highly sensitive to external stimuli, including temperature, electric fields, and optical excitation, enabling multiple control modalities for device applications.



The practical implementation of VO₂ in functional devices critically depends on the ability to precisely control its phase transition characteristics, which are intimately linked to the material's synthesis and processing conditions. Various fabrication methods, including physical vapour deposition, chemical vapour deposition, and solution-based approaches, produce VO₂ with distinct microstructural features that profoundly influence its MIT behaviour [3],[13],[14]. Key parameters such as crystallinity, stoichiometry, strain state, and defect concentration are largely determined by the synthesis technique and processing parameters. For instance, oxygen non-stoichiometry can introduce charge carriers that modify the transition temperature, while epitaxial strain from lattice-mismatched substrates can stabilise intermediate phases or shift T_i by tens of degrees. Additionally, nanoscale confinement effects become prominent in low-dimensional VO₂ structures, where surface and interface contributions can significantly alter the transition thermodynamics [1].

Understanding the relationship between synthesis methods and phase transition properties is essential for optimising VO₂'s performance in specific applications. Different deposition techniques offer varying degrees of control over critical material parameters - while physical vapour deposition methods like pulsed laser deposition can produce high-quality epitaxial films with sharp transitions, they often lack scalability [15],[16]. Conversely, chemical and solution-based methods may be more suitable for large-area applications but typically introduce more defects and heterogeneity [17]. The growing interest in VO₂-based devices has driven the development of novel synthesis approaches that combine the advantages of multiple techniques while mitigating their limitations. Recent advances in atomic layer deposition and hybrid processing methods have enabled unprecedented control over VO₂'s structural and electronic properties at the nanoscale.

This review systematically examines the various synthesis methods for VO₂ and their impact on the material's phase transition characteristics. By critically analysing the relationship between fabrication techniques, structural properties, and MIT behaviour, we aim to provide a comprehensive resource for researchers seeking to optimise VO₂ for specific applications. The discussion encompasses fundamental aspects of phase transition chemistry, detailed comparisons of synthesis methodologies, and their respective influences on transition temperature, hysteresis, and switching dynamics. Ultimately, this work seeks to establish structure-property-processing relationships that can guide the rational design of VO₂-based materials with tailored performance characteristics for advanced technological applications.

2. Phase Transition Chemistry of VO₂

The metal-insulator transition (MIT) in vanadium dioxide (VO₂) is a complex phenomenon governed by coupled electronic and structural transformations. Below the critical transition temperature (T_i ≈ 68°C), VO₂ exists in a low-temperature monoclinic phase (M1, space group P2₁/c), which is insulating, while above T_i, it transitions to a high-temperature tetragonal rutile phase (R, space group P4₂/nm), exhibiting metallic conductivity [4],[18],[19]. This transition is driven by strong electron-electron correlations (Mott-Hubbard mechanism) and structural distortions (Peierls instability), making VO₂ a prototypical correlated electron material. The transmission diagram can be seen in Figure 1:

2.1. Electronic Transition Mechanism

In the insulating M1 phase, vanadium (V⁴⁺) ions undergo dimerisation along the *c*-axis, resulting in a pairing distortion that splits the degenerate *d*// orbitals (*d_{x²-y²}*) into bonding and antibonding states. This Peierls-like distortion, combined with strong on-site Coulomb repulsion (*U*), opens a Mott-Hubbard gap (~0.6 eV), rendering the material insulating [21],[22]. The electronic transition can be represented by the following charge disproportionation reaction in (1):



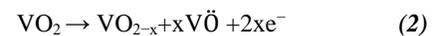
Above T_i, the V-V dimers dissociate, leading to a delocalisation of *d*-electrons and the collapse of the bandgap. The metallic R phase is characterised by overlapping *d*// bands, resulting in enhanced electrical conductivity.

2.2. Structural Transition Mechanism

The M1-to-R transition involves a cooperative distortion of the VO₆ octahedra [23]. In the M1 phase, the vanadium chains exhibit alternating short (≈ 2.65 Å) and long (≈ 3.12 Å) V-V distances due to dimerisation, while the R phase adopts a symmetric rutile structure with uniform V-V spacing (≈ 2.87 Å). The structural transformation is accompanied by a significant unit cell volume change (~1%), which contributes to the first-order nature of the transition.

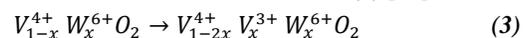
2.3. Key Factors Influencing the MIT

- **Stoichiometry and Defects:** Oxygen non-stoichiometry (VO₂ ± x) introduces point defects such as oxygen vacancies (V_o) or interstitials (O_i), which perturb the electronic structure and alter T_i [24]. For example, oxygen-deficient VO₂ tends to exhibit a reduced T_i due to increased electron doping shown in (2):



Where V \ddot{O} denotes a doubly charged oxygen vacancy.

- **Epitaxial Strain:** Substrate-induced strain can stabilise metastable phases (e.g., the M2 or T phase) or shift T_i. Compressive strain typically lowers T_i, while tensile strain may increase it. For instance, VO₂ grown on TiO₂ (001) experiences compressive strain, reducing T_i by up to 20°C [25].
- **Doping Effects:** Cation substitution (e.g., W⁶⁺, Mo⁶⁺, Ti⁴⁺) can significantly modulate T_i. Tungsten doping (W⁶⁺) is particularly effective, decreasing T_i by ~20–25°C per at% W due to electron donation shown in (3) [26]:



Conversely, aliovalent dopants like Al³⁺ or Cr³⁺ increase T_i by introducing hole carriers.

- **Grain Size and Morphology:** Nanocrystalline VO₂ exhibits a broadened MIT due to surface and interface effects [27]. Quantum confinement in nanoparticles (< 20 nm) can suppress the transition entirely, while mesoporous films show reduced thermal hysteresis.



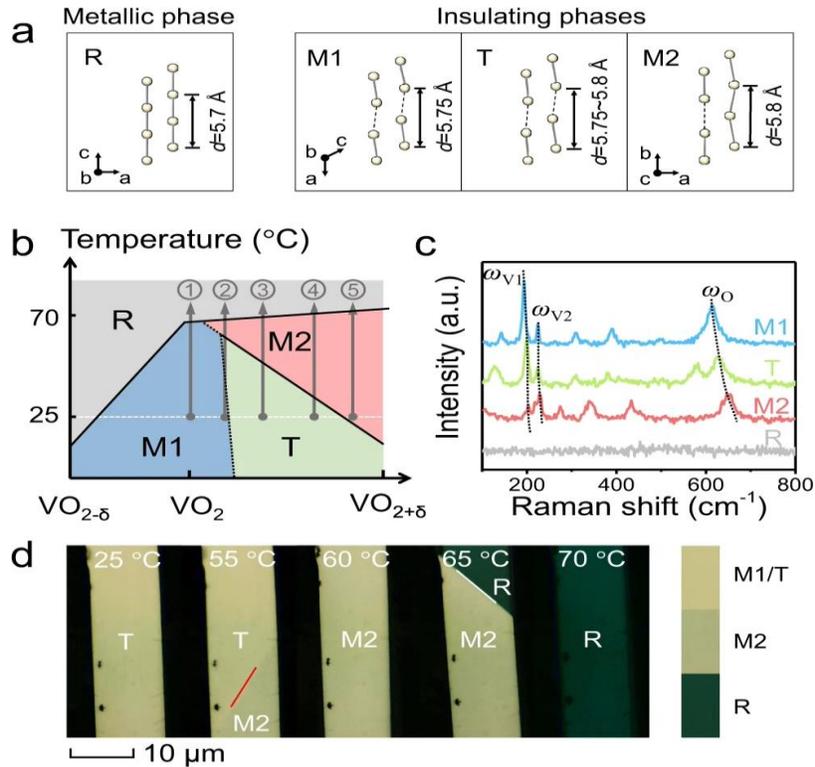


Figure 1: (a). Schematics of the arrangement of V ions in different VO_2 phases (M1, T, M2, and R). The solid circles represent the V ions, solid lines represent a short V–V distance of $<0.3 \text{ nm}$, and dash lines connect the neighboring V ions with a V–V distance of $>0.3 \text{ nm}$. (b). Schematics of stoichiometry–temperature phase diagram for VO_2 crystals. The gray, blue, green, and red regions in the diagram represent the R phase, M1 phase, T phase, and M2 phase, respectively. The gray arrows (routes 1–5) trace the phase evolution process of VO_2 with various oxygen contents from room temperature, (c). Characteristic Raman spectra of VO_2 phases. Dash lines trace ω_{V1} , ω_{V2} , and ω_O phonon frequencies in the Raman spectra and (d). Temperature-dependent optical images of a single VO_2 beam upon heating, revealing its whole domain evolution process corresponding to route 3 of b. The red line shows the position of the domain wall between T and M2 phases, while the white line shows the position of the M2–R domain wall [20].

2.4. Summary of Phase Transition Chemistry

The MIT in VO_2 is a delicate interplay of electronic correlation, lattice dynamics, and defect chemistry. Precise control over stoichiometry, strain, and doping is essential for tailoring the transition properties for specific applications. The following Table 1 summarises key chemical and structural aspects of the MIT:

Table 1:
Chemical and structural aspects of the MIT

Parameter	M1 Phase (Insulating)	R Phase (Metallic)
Crystal Structure	Monoclinic ($P2_1/c$)	Tetragonal Rutile ($P4_2/mmm$)
V–V Dimerization	Present ($2.65 \text{ \AA} / 3.12 \text{ \AA}$)	Absent (uniform 2.87 \AA)
Bandgap	$\sim 0.6 \text{ eV}$ (Mott–Hubbard)	Closed (metallic)
Dominant Mechanism	Peierls + Mott–Hubbard	Band overlap

3. Synthesis Methods and Their Impact on Phase Transition Properties

The synthesis of vanadium dioxide (VO_2) is a critical factor in determining its metal–insulator transition (MIT) characteristics, as different fabrication techniques produce materials with distinct structural, morphological, and electronic properties. The choice of synthesis method influences key parameters such as crystallinity, stoichiometry, grain size, and defect concentration, all of which play crucial roles in modulating the transition temperature (T_1), hysteresis width, and switching sharpness. This section provides a detailed examination of various synthesis approaches and their specific effects on VO_2 's phase transition behaviour.

3.1. Physical Vapour Deposition (PVD) Methods

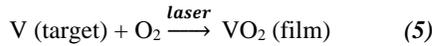
Among physical deposition techniques, magnetron sputtering and pulsed laser deposition (PLD) are widely used for VO_2 thin film fabrication [28]. Magnetron sputtering, which involves reactive deposition of vanadium in an oxygen–argon atmosphere, offers excellent control over film stoichiometry through precise regulation of oxygen partial pressure. The process can be described by (4):



The process typically requires post-deposition annealing at $400\text{--}500^{\circ}\text{C}$ to achieve optimal crystallinity, with the resulting films exhibiting well-defined MIT characteristics. However, defect formation, particularly oxygen vacancies, can lead to hysteresis



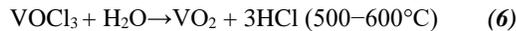
broadening, while stress accumulation in thicker films may cause mechanical failure. PLD, utilising laser ablation of a vanadium target in an oxygen environment, produces highly epitaxial films with exceptionally sharp transitions ($\Delta T < 5^\circ\text{C}$) [29]. PLD utilises laser ablation of a vanadium target in an oxygen background as shown in (5):



The technique allows for strain engineering through substrate selection, with Al_2O_3 and TiO_2 being common choices for modulating T_i . Despite its superior film quality, PLD suffers from limitations in deposition area and high equipment costs, making it less suitable for large-scale applications.

3.2. Chemical Vapour Deposition (CVD) Techniques

Chemical vapour deposition methods, including atmospheric-pressure CVD (APCVD) and metal-organic CVD (MOCVD), provide alternative routes for VO_2 synthesis. APCVD employs halide precursors such as VOCl_3 at elevated temperatures ($500\text{--}600^\circ\text{C}$), resulting in polycrystalline films with grain size dependent on deposition temperature [30]. APCVD employs halide precursors at elevated temperatures, as in (6):



While higher temperatures improve crystallinity and reduce T_i , the method often produces films with significant surface roughness and challenges in thickness control below 50 nm. MOCVD, using organometallic precursors like vanadyl acetylacetonate, operates at lower temperatures ($300\text{--}450^\circ\text{C}$) and enables conformal coatings on complex geometries [31]. MOCVD uses organometallic precursors as in (7):



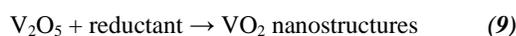
However, carbon incorporation from precursor decomposition can reduce T_i by $10\text{--}15^\circ\text{C}$ and may introduce electronic defects. Both CVD approaches offer better scalability than PVD methods but require careful optimisation to minimise impurities and defects that could degrade MIT performance.

3.3. Solution-Processed Methods

Solution-based synthesis techniques, including sol-gel and hydrothermal methods, present cost-effective alternatives for VO_2 preparation. The sol-gel process involves hydrolysis-condensation of vanadium alkoxides followed by high-temperature annealing ($>500^\circ\text{C}$), yielding materials with broadened hysteresis (ΔT up to 30°C) due to high defect concentrations [32],[33]. Nanoparticle size effects become prominent below 20 nm, with quantum confinement potentially suppressing the MIT entirely. Involves hydrolysis-condensation of vanadium alkoxides, as can be seen in (8):



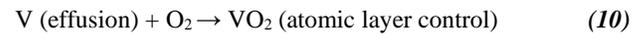
Hydrothermal synthesis, conducted in aqueous solutions at elevated pressures, produces various nanostructures such as nanowires and nanorods [13],[34]. Autoclave-based crystallisation can be seen in (9):



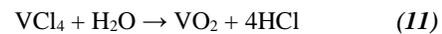
These materials exhibit anisotropic MIT behaviour and size-dependent transition characteristics, with surface defects often mediating transition broadening. While solution methods offer advantages in scalability and nanostructure control, they typically require post-synthesis treatments to achieve the desired stoichiometry and crystallinity, and may introduce organic residues that affect electronic properties.

3.4. Advanced Deposition Techniques

Molecular beam epitaxy (MBE) and atomic layer deposition (ALD) represent the state-of-the-art in precision VO_2 fabrication. MBE provides atomic-level control under ultra-high vacuum conditions, producing films with atomically sharp interfaces and extremely narrow hysteresis ($<1^\circ\text{C}$) [35]. Ultra-high vacuum growth, as can be seen (10):



This method enables fundamental studies of strain and interface effects but suffers from prohibitively low growth rates and high costs. ALD, based on self-limiting surface reactions, offers exceptional conformality and thickness control at the Angstrom level, making it ideal for coating high-aspect-ratio structures [36]. Self-limiting surface reactions as in (11):



However, ALD-grown VO_2 often contains amorphous components that lower T_i , and may incorporate halide impurities from precursors. These advanced techniques, while not yet suitable for mass production, provide invaluable insights into structure-property relationships and serve as benchmarks for material quality.

The following Table 2 summarises key synthesis techniques and their effects on VO_2 phase transition properties.

4. Key Challenges and Future Perspectives in VO_2 Research

Despite significant advancements in the synthesis and characterisation of VO_2 , several critical challenges persist that limit its practical implementation in next-generation devices.

4.1. Current Challenges

- **Stoichiometric Precision:** Maintaining exact VO_2 stoichiometry remains challenging, as oxygen vacancies (VO'') and non-stoichiometric phases ($\text{VO}_2 \pm \delta$) dramatically influence the metal-insulator transition (MIT) characteristics, including transition temperature (T_c), hysteresis width, and switching dynamics. Even minor deviations ($\delta > 0.01$) can suppress the MIT or induce intermediate phases.
- **Scalability Limitations:** While high-precision techniques like molecular beam epitaxy (MBE) and pulsed laser deposition (PLD) yield superior single-crystalline films with sharp transitions, their low throughput and high costs hinder industrial adoption. Alternative methods, such as chemical vapour deposition (CVD), offer better scalability but often compromise on film quality and transition sharpness.



Table 2:
Effects of synthesis techniques on VO₂ phase transition

Synthesis Method	Crystallinity	Typical T _t (°C)	Hysteresis Width	Key Advantages	Key Challenges
Magnetron Sputtering	Polycrystalline/Epitaxial	60–75	5–15°C	Scalable, tunable strain	Defects, requires annealing
PLD	Highly Epitaxial	65–70	1–5°C	High-quality films	Expensive, small area
APCVD	Polycrystalline	65–75	10–20°C	Good uniformity	Rough morphology
MOCVD	Polycrystalline	50–70	10–25°C	Conformal coatings	Carbon contamination
Sol-Gel	Nanoporous/Polycrystalline	60–80	15–30°C	Low cost, scalable	High defects, broad hysteresis
Hydrothermal	Nanostructured	40–70	10–40°C	High surface area	Stoichiometry control difficult
MBE	Single-crystal Epitaxial	~68	<1°C	Ultra-precise	Extremely costly
ALD	Amorphous/Nanocrystalline	50–65	10–20°C	Atomic-level control	Low crystallinity

- **Precise Property Tuning:** Although doping (e.g., W⁶⁺, Mo⁶⁺) and strain engineering can modulate T_c, achieving predictable and uniform property control across large-area samples remains difficult. Substrate-induced strain, in particular, can lead to inhomogeneous phase distributions and metastable intermediate states (e.g., M2 or T phases).
- **Interface and Substrate Effects:** In thin-film architectures, interfacial reactions, lattice mismatch, and thermal expansion differences can dominate MIT behaviour, often masking intrinsic material properties. This is especially problematic for heterostructure integration in device applications.

4.2. Future Research Directions

To address these challenges, future efforts should prioritise:

- **Low-Temperature Synthesis:** Developing growth techniques that enable high-quality VO₂ deposition below 300°C would facilitate integration with flexible substrates (e.g., polymers) and temperature-sensitive device architectures. Plasma-enhanced atomic layer deposition (PE-ALD) and photochemical solution processing are promising avenues.
- **Defect Engineering:** Advanced characterisation techniques (e.g., in-situ TEM, XAS) combined with computational modelling can help establish defect-property relationships, enabling targeted mitigation of oxygen vacancies and grain boundary effects that broaden hysteresis.
- **Hybrid Fabrication Strategies:** Combining the strengths of different methods, such as ALD for interfacial control, followed by CVD for bulk growth, could provide an optimal balance between scalability and film quality. Additionally, additive manufacturing approaches may enable novel VO₂ nanostructuring.
- **Device-Oriented Optimisation:** Future work should focus not only on fundamental material properties but also on integration challenges, including contact engineering, in-

terfacial stability, and cycling endurance for practical applications in memristors, smart coatings, and thermal switches.

5. Conclusion

The phase transition properties of VO₂ are highly sensitive to the synthesis method, which affects stoichiometry, strain, and microstructure. Physical deposition techniques (sputtering, PLD) yield high-quality films with sharp transitions, while solution-based methods offer scalability at the cost of broader hysteresis. Understanding the interplay between synthesis conditions and MIT behaviour is crucial for optimising VO₂ for applications in smart coatings, sensors, and electronic devices. Future advancements in defect control and strain engineering will further enhance the performance of VO₂-based technologies.

Declaration

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