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# A review of the preparation, properties and applications of $VO_2$ thin films with the reversible phase transition

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The reversible phase transition of vanadium dioxide under thermal, electrical, and optical stimuli is the enabling concept for the functioning of smart materials and is the basis for the development of various device materials such as optical, electrical, thermal, and mechanical devices based on $VO_2$ on rigid and flexible platforms. The phase transition temperature of $VO_2$ near room temperature is considered an excellent choice and a potential candidate to replace traditional materials in a variety of applications. There is a growing interest in $VO_2$ applications for a wide range of devices, and the use of $VO_2$'s structure to manipulate and explore the functions of various application devices, as well as the modification of $VO_2$ structures to improve performance in a variety of materials, can lead to extremely exciting innovations. A lot of effort has been put into the challenges of practical production and practical application, and it is necessary to find an industrially feasible manufacturing method for the preparation of $VO_2$ films, which is the basis for the practical application of $VO_2$-based equipment. Based on this background, we first briefly describe the structure of $VO_2$, the phase transition mechanisms involved, and the factors and other properties induced by the phase transition of $VO_2$. Then, the current status and advantages and disadvantages of $VO_2$ thin film preparation technologies are introduced in detail, including pulsed laser deposition (PLD), magnetron sputtering, the sol-gel method, and chemical vapour deposition (CVD). In addition, we propose three strategies to improve the performance of $VO_2$ thin films, including element doping, multi-layer composites, and surface structure. We also discussed the different applications of $VO_2$ under thermal, electrical, and light stimulation, as well as the development trends and future challenges of $VO_2$ thin films.

KEYWORDS

**$VO_2$ films, phase transition, preparation technology, modification, application**

# 1 Introduction

In 1959, Morin discovered that vanadium dioxide ($VO_2$) in the Bell laboratory has unique and reversible metal-insulator phase transformation characteristics (WITH) (Morin, 1959), and $VO_2$ undergoes a structural phase transition (SPT), that is, from a low-temperature monoclinic rutile structure to a high-temperature tetragonal rutile structure. With the transformation of the crystal structure, $VO_2$'s optical and electrical properties will be mutated, so in the following decades, a large number of researchers have been interested in $VO_2$. The film was thoroughly studied (as shown in Figure 1).

Although there are quite a few other transition metal oxides (Adler, 1968), such as $Mo_9O_{26}$, $Fe_3O_4$, $VnO_{2n-1}$, $Ti_2O_3$. They also have this MIT phase transition property. However, in comparison, the phase transition temperature of $VO_2$ is closest to room temperature. The phase transition temperature can be further adjusted by doping elements such as W, F or Mo. This unique property near room temperature makes $VO_2$ a photoelectric switching material (Lysenko et al., 2006), chromic coating (Manning et al., 2004), infrared imaging, and many other fields have broad application prospects.

Vanadium has a unique 3D orbital hybridization in its chemical bonds, which makes it exhibit multivalence properties, so vanadium has a wide range of oxide types, including VO, $V_2O_3$, $VO_2$, and $V_2O_5$ and 12 others. In these 12 vanadium oxides, $VO_2$ and $V_2O_5$ have the chemical stability required for microelectronic devices, so the characteristic, mechanism, and application research of MIT mainly focuses on $VO_2$ and $V_2O_5$, two vanadium oxides. Among them, the phase transition temperature of $VO_2$ is 68°C, which is closer to room temperature and has greater application potential in thermal control, so the research on $VO_2$ is more extensive. Since

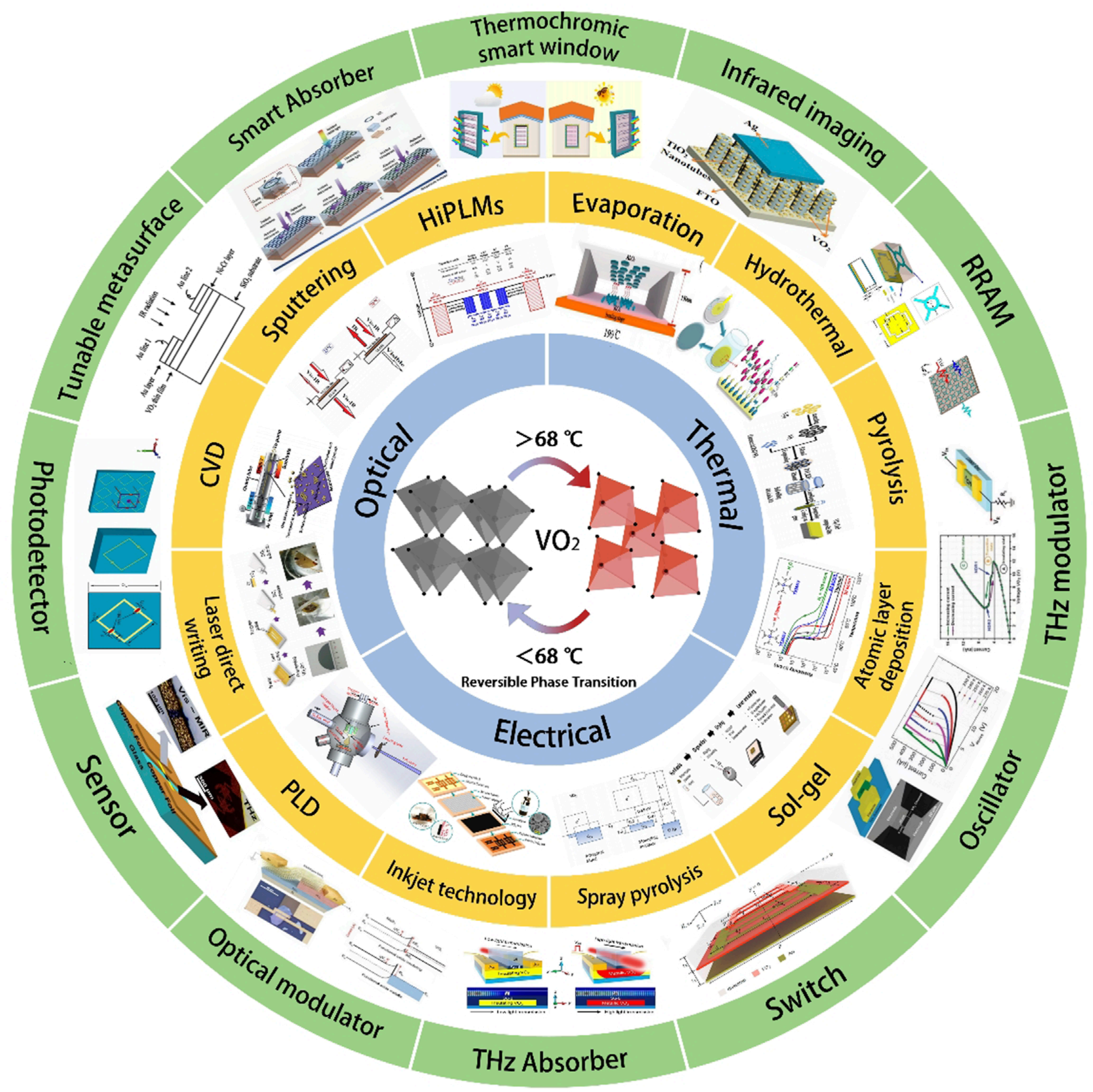


FIGURE 1
Preparation and application of $VO_2$-based films.

the V ion in $VO_2$ is not the highest valence state, it is difficult to guarantee that a high-purity $VO_2$ film can be prepared. Therefore, how to prepare high-purity and high-quality $VO_2$ films is a key problem that limits their application. The quality of $VO_2$ films is directly related to the excellent performance of the device, which requires researchers to select appropriate preparation technology, optimize the process according to the application requirements of the device, and finally obtain high-quality $VO_2$ films. Therefore, the study of the preparation technology of $VO_2$ films is a foundational step for subsequent application development, and it is of great research significance. At present, the preparation process of $VO_2$ film mainly includes magnetron sputtering (Luo and Huang, 2010), the sol-gel method (Chae et al., 2006; Li et al., 2015), chemical vapor deposition (Vernardou et al., 2006), the pulsed laser deposition method (Cole et al., 1997; Bukhari et al., 2020) and others. The conditions required for the preparation of $VO_2$ thin films are different, so researchers at home and abroad have conducted detailed research on the preparation process of $VO_2$ films to find out the best preparation scheme.

Therefore, in this paper, based on the background of $VO_2$ preparation and application, i) we introduce the structural characteristics and phase transition mechanisms of $VO_2$ materials in the second part, ii) discuss the factors that induce the phase transition of $VO_2$, the types of phase transitions, and the changes in other characteristics of $VO_2$, iii) focus on the advantages and disadvantages of four vanadium dioxide film preparation technologies, iv) relate to gas-phase synthesis and liquid-phase synthesis, and propose three $VO_2$ modification strategies to achieve the purpose of regulating the performance of $VO_2$. v) We list five popular applications according to the different thermal, electrical, and optical stimulation signals, finally put forward the challenges faced by $VO_2$ films, and look forward to the direction of $VO_2$ preparation and application.

# 2 Introduction to $VO_2$ phase change materials

## 2.1 Crystal structure and band structure

Vanadium is located in the fifth subgroup of the fourth period. As a typical transition metal element, it can combine with oxygen to form 13 oxides. $VO_2$ is a strong electron-related material, and the crystal structure of $VO_2$ will vary depending on the preparation method, including $VO_2$ (R), $VO_2$ (M1), $VO_2$ (M2), $VO_2$ (A), $VO_2$ (B), $VO_2$ (C), $VO_2$ (D), $VO_2$ (T), etc. These different crystal structures differ greatly in some physical properties, such as electron band structure, phase transition temperature, infrared transmission and regulation characteristics, density, specific heat capacity, and thermal conductivity (Figure 2).

### 2.1.1 Crystal structure

As shown in Figures 3A, B, at 68°C, $VO_2$ undergoes a metal-semiconductor structure transition (MIT) from a low-temperature monoclinic (M1) to a high-temperature rutile (R) phase, during which the lattice structure changes and the conversions are reversible. When the temperature is higher than 68°C, $VO_2$ behaves as a metallic R phase, which is in the $P_{42}/mnm$ space point group. V atoms occupy the positions of the apex and body center of the unit cell; each V atom and the adjacent six oxygen atoms form a regular octahedral structure. The lattice constants are $a_r = b_r = 4.55$ Å and $c_r = 2.85$ Å. When the temperature is lower than 68°C, $VO_2$ behaves as an insulating M1 phase, which is in the $P_21/c$ space point group. Compared with the $VO_2$ structure of the metal R phase, the V atom moves from the center of the octahedron to the surface, deviating from the apex and body center position of the unit cell; the β angle changes from 90° to 122.6° and the V-O octahedron also changes from a regular octahedron to a hemioctahedron. Thus, the highly symmetrical quadrilateral structure changes to a low-symmetrical monoclinic structure, and the lattice constant becomes $a_{m1} = 5.75$ Å and $b_{m1} = 4.53$ Å, $c_{m1} = 5.38$ Å.

### 2.1.2 Band structure

In the process of phase transition, in addition to the changes of crystal structure, the changes of band structure also occur (Figure 3C). When $VO_2$ is in the high-temperature metallic phase, the $d_{II}$ orbital and the $\pi^*$ orbital overlap, the $\pi^*$ orbital is partially filled with electrons, and the Fermi energy level is located in the two orbitals. When the temperature is lower than 68°C, the V atoms are displaced along the $c_r$ axis to form a jagged V-V structure, which aggravates the hybridization of the 3d orbital of V and the 2p orbital of O, resulting in the upward shift of the $\pi^*$ orbital, and the electrons in the $\pi^*$ orbital are transferred to the $d_{II}$ orbital due to the greater mobility, and the $d_{II}$ orbital splits into a full-band $d_{II}$ orbital and an empty $d_{II}^*$ orbital, at which point $VO_2$ transforms into a semiconductor monoclinic structure, which behaves as an insulating phase.

During the MIT conversion of $VO_2$, the specific changes in the band structure from the rutile phase to the monoclinic phase are as follows: 1) The increase of the $\pi^*$ band above the Fermi level $E_F$ (relatively decreasing $E_F$ and distributed below the $\pi^*$ band) leads to the full state of $d_{II}$. 2) The band splits into two bands. This phenomenon of separating states increases the activation energy of the semiconductor insulation state to a certain extent.

## 2.2 Phase transition mechanism

At present, there are three main explanations for the phase transition mechanism of $VO_2$, namely, the Mott-Hubbard phase transition driven by strong electron correlation, the Peierls phase transition driven by the change of the lattice structure, and the synergistic coupling of Mott-Hubbard and Peierls mechanism.

It is believed that structural changes are what drive Peierls' phase-transformation mechanism. The occurrence of the band gap in the low-temperature semiconductor state is due to the lattice distortion of the monoclinic phase; that is, the phase transition is caused by the instability of the crystal lattice. Budai et al. (Budai et al., 2014) used X-ray and neutron scattering techniques to discover the driving effect of non-harmonic phonons during the phase transition of $VO_2$ (Figure 4B), confirming the decisive role of lattice distortion in the phase transition process. Cavalleri's (Cavalleri et al., 2004) experiments using ultrafast spectroscopy have shown that the $VO_2$ low-temperature insulator may have

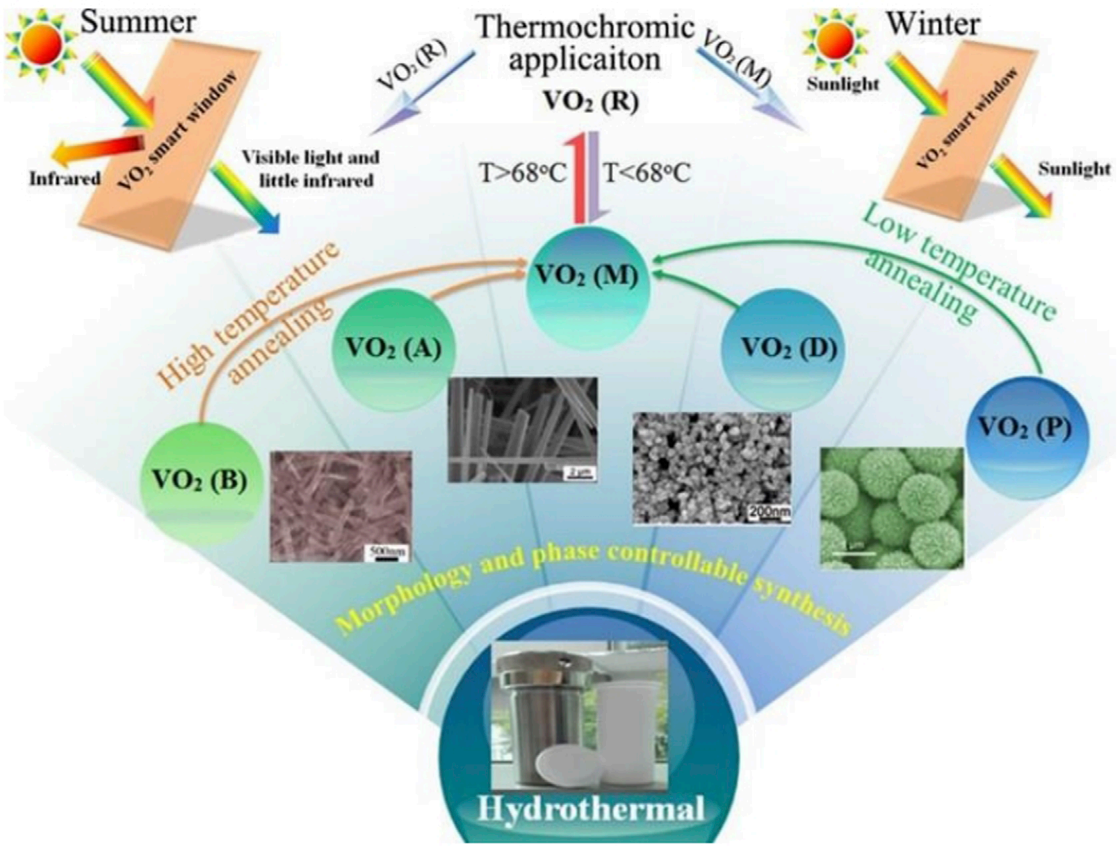


FIGURE 2
Crystalline structure and properties of $VO_2$ (M. Lie et al., 2017).

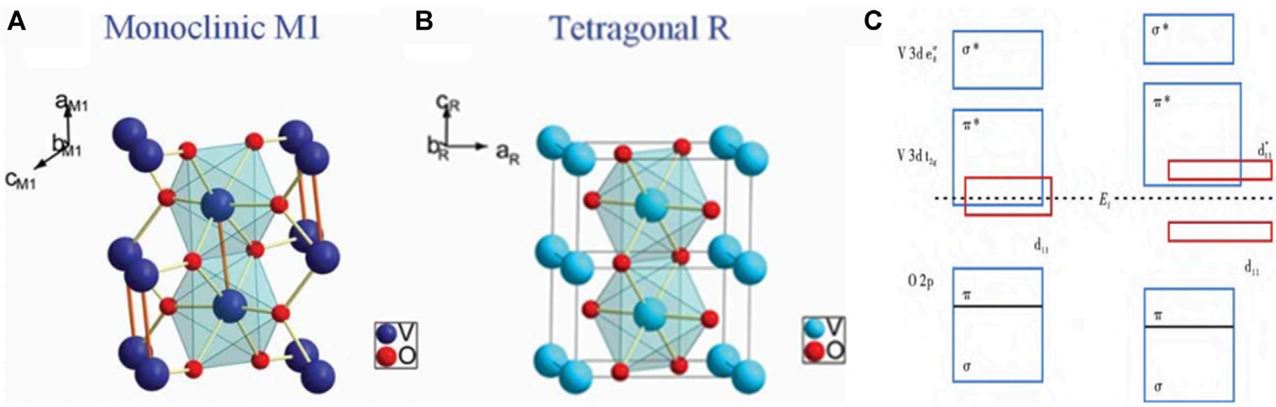


FIGURE 3
Lattice structure of $VO_2$ at low temperature M phase **(A)** and **(B)** high temperature R phase (Wu et al., 2013); **(C)** Band structure changes between $VO_2$ R phase and M phase (Eyert, 2002).

important band-like properties, and the band-like properties of the low-temperature insulator are caused by the distortion of Peierls, which further indicates that the MIT phase transition of $VO_2$ is due to the structure-driven.

When the electron spacing of the crystal shrinks, the upper and lower Hubbard bands overlap and are not satisfied, which is a metallic phase. When the upper and lower Hubbard bands are empty and full, they are insulated. This change in the electron spacing

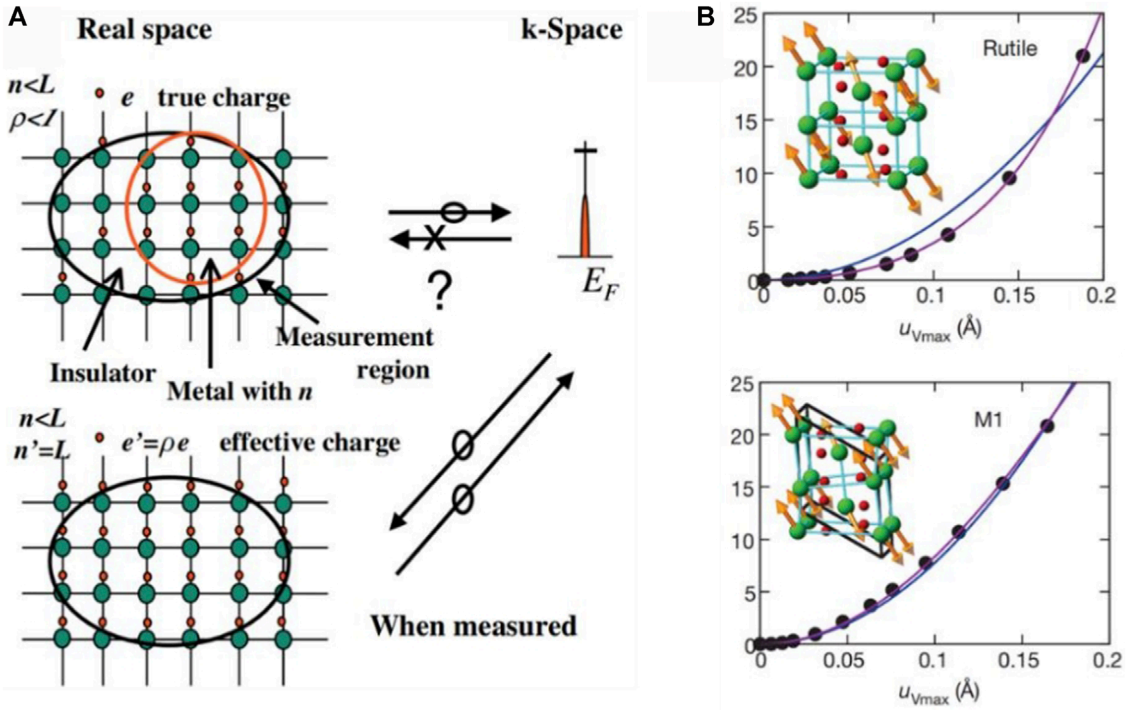


FIGURE 4
Mott phase change and Peierls phase change: **(A)** Mott A phase transition due to a change in the concentration of electrons in a phase transition; **(B)** Peierls Phase change V-V Phase transitions due to pairing and lattice distortion (Kim et al., 2004).

affects the electron interaction, so that the overlapping state of the upper and lower Hubbard bands changes, and the process that determines the MIT transition is called the Mott-Hubbard phase transition (Mott, 1949). The phase transition theory suggests that the strong correlation between electrons is the dominant factor in the $VO_2$ phase transition, which is independent of the change of lattice structure. According to the Mott band theory model, when the concentration of free electrons exceeds a certain concentration, additional electrons in different localized areas will be generated, allowing the material to exhibit metallic properties. When the system has been transformed into a metallic feature, its structure remains in the monoclinic phase (Figure 4A).

Since both the Peierls phase transition theory and the Mott-Hubbard phase transition theory have their own limitations, it is impossible to explain all experimental phenomena with a single theoretical model. As research continues to deepen, more and more people think that SMT is the result of the Peierls phase transition and the Mott-Hubbard phase transition synergy. Yao (Yao et al., 2010) studied MIT transitions. It is found that the curves of V-V coordination twist angle and resistance under temperature change are almost consistent, and it is believed that the electron-lattice distortion combined effect changes the band gap. Paquet (Paquet and Leroux-Hugon, 1980) proposed a phase transition model based on electron-electron interaction and lattice distortion, concluded that the phase transition at temperature is dominated by the strong interaction between electrons, and the two d-bands with overlapping Fermi levels of metallic phases depend on the influence of lattice distortion.

## 2.3 Factors that induce $VO_2$ phase transition

A common method for inducing MIT is thermal triggering and changing the temperature by heating or cooling. Figure 5A shows that when the temperature rises from 341 K to 344 K, the resistance of the $VO_2$ film decreases by almost four stops (Tokura, 2003). Other methods of triggering a phase change include electricity (Miyano et al., 1997; Qazilbash et al., 2007), optics (Qazilbash, 2007; Tokura, 2003), magnetism (Qazilbash et al., 2007) and strain (Cao et al., 2009). Examples of each method are shown in Figures 5B–E.

Thermally induced phase transition is the most common way to induce a phase transition of $VO_2$, which is triggered when the outside temperature rises to the phase transition temperature. In this process, the lattice structure, optical constant (refractive index n, extinction coefficient k), and conductivity of $VO_2$ are abruptly changed. This thermotropic property can be applied to heat-activated devices.

There are two ways to explain electro-induced phase transitions. One view is that holes and electrons introduced by the electric field cause the phase transition of $VO_2$, while another view is that the electrolytically induced phase transition of $VO_2$ is due to Joule heating or electric heating, which is achieved by the local melting of the insulator when an electric current flows through $VO_2$.

In 2000, for the first time, Stefanovich (Stefanovich et al., 2000) reported that the reversible phase transition of $VO_2$ can be triggered by applying bias and electron injection. Kim (Lee et al., 2017)

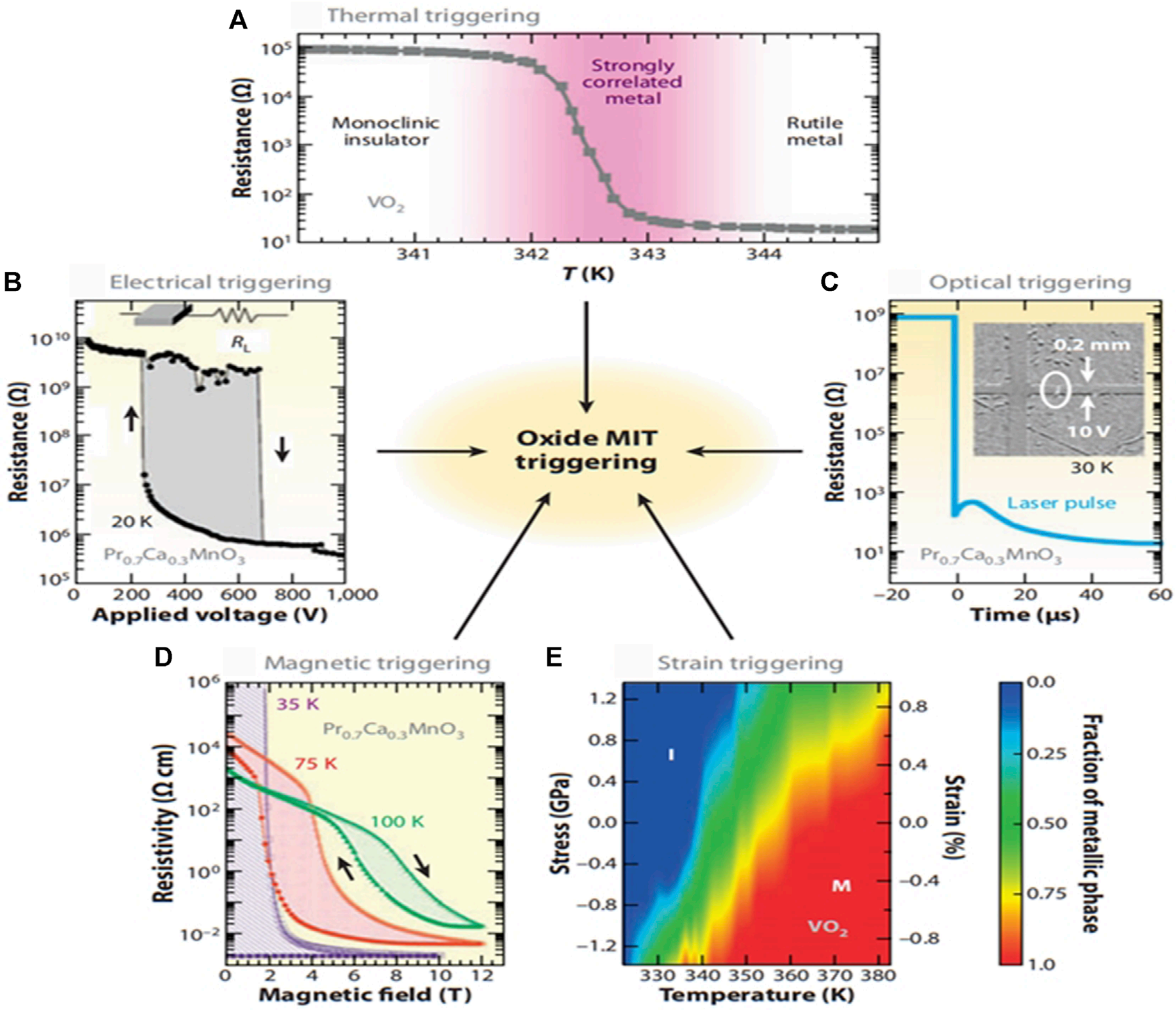


FIGURE 5
MIT triggering methods for relevant oxides: **(A)** temperature-triggered MIT in $VO_2$ (Qazilbash et al., 2007); **(B)** electrical triggering (Tokura, 2003); **(C)** optical triggering (Tokura, 2003); **(D)** magnetic triggering (Tokura, 2003); **(E)** Effect of strain/stress on MIT in $VO_2$ (J. Cao et al., 2009).

reduced the critical voltage that triggers the $VO_2$ phase transition by increasing the temperature. Wang (Bae et al., 2013) fabricated $VO_2$ two-terminal devices using $VO_2$ nanowires and successfully transformed $VO_2$ from an insulating phase to a metallic phase with a bias voltage of 0.34 V. The phase transition was triggered by Joule heating generated by an electric current.

Chen (Chen et al., 2015a) prepared $VO_2$ epitaxial crystal films on p-GaN (001) substrate by metal-organic chemical vapor deposition (MOCVD), and formed an ideal P-N junction. A bias voltage is applied to the P-N junction, and the phase change modulation of the $VO_2$ film is realized by carrier/electron density control.

In recent years, the study of the laser response and phase transition principle of $VO_2$ has become more and more important. Laser-induced phase transitions cause band collapse by changing the electron correlation instantaneously and finally stabilize through structural evolution.

In 1971, Roach (Roach and Balberg, 1971) and his team showed that ultrafast lasers can effectively excite the reversible phase transition of $VO_2$, a process that is thought to be an energy conversion process between photons and phonons. Cavalleri (Cavalleri et al., 2001) used femtosecond lasers and visible light pulses to study the electrodynamic characteristics of crystal structure change during photoinduced phase transitions and found that when the laser flux increases to a certain size, $VO_2$ can induce a structural transition from the insulating monoclinic phase to the metallic rutile phase.

## 2.4 Physical, optical, electrical and other properties of $VO_2$

The physical, optical, electrical, and other properties of $VO_2$ also show great variation. Its characteristics change as shown in Figure 6. The phase transition in $VO_2$ can be triggered by stimuli of various types, such as heat, light, electrical, chemical, mechanical, magnetic, etc. The reconfigurable and reversible phase transition by a single-stimulus or multi-stimuli and the dynamically

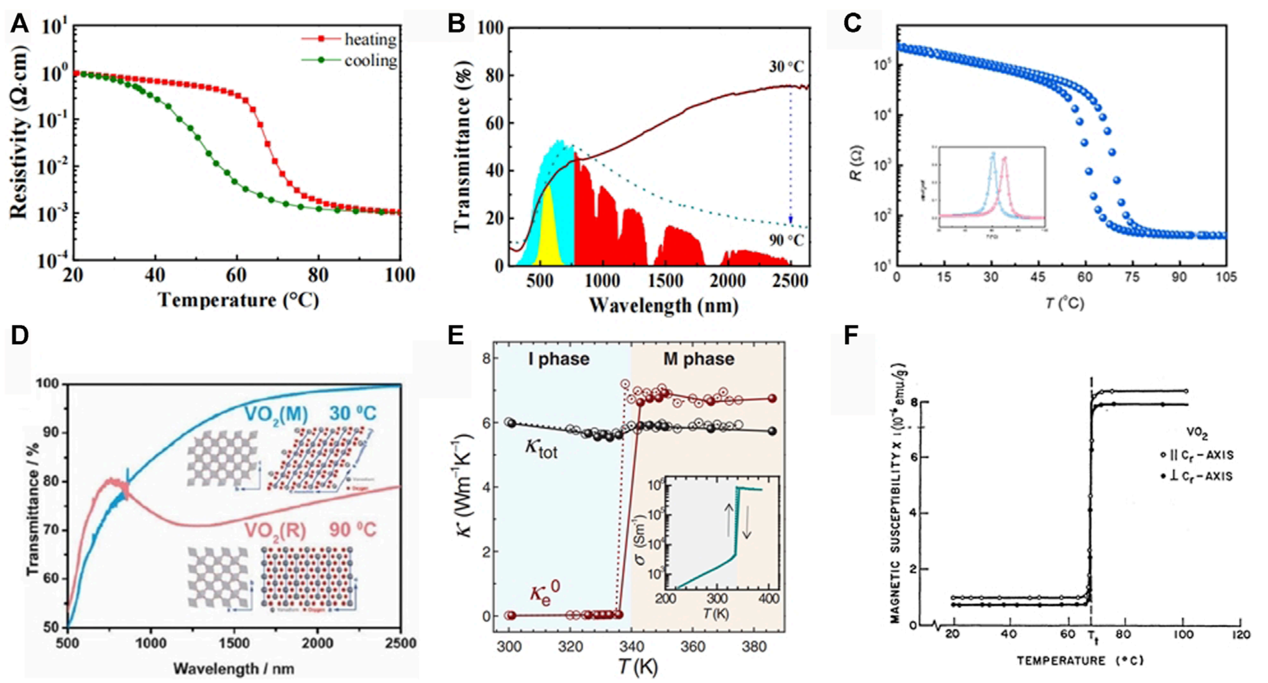

FIGURE 6
$VO_2$ performance changes: **(A)** Resistivity of $VO_2$ films as a function of temperature, Occurs before and after the $VO_2$ phase transition (Wu et al, 2013); **(B)** Transmission spectra of $VO_2$ films before and after phase transition (Berglund and Guggenheim, 1969); **(C)** Electricity (Li et al., 2016); **(D)** Optics (Li and Dho, 2011); **(E)** Thermodynamics (Xu et al., 2005); **(F)** Magnetism (Fu et al., 2013).

tunable optical properties in a broad range of wavelengths (λ) are the superior features facilitating $VO_2$ in smart windows, optical switching, modulator, sensor, nanoactuator, sensor, smart radiator, transistor, oscillator applications, and so on.

When the temperature rises to the phase transition point, $VO_2$ transforms into a tetragonal rutile phase structure with a bandgap of variable conductivity, showing metallic properties, and strong absorption and reflection of low-frequency infrared light, but the transmittance of visible light remains basically unchanged. Before and after the phase transition, the transmittance of the $VO_2$ film remained basically unchanged in the visible band and showed an obvious mutation in the infrared band (Figures 6B, D).

Relevant studies have shown that the $VO_2$ thermal conductivity of high-temperature metal phases is significantly improved compared to $VO_2$ at room temperature, and the $VO_2$ thermal conductivity of metal phases can reach 6 W/MK (Figure 6E).

As shown in Figure 6F, the M1 phase $VO_2$ at room temperature is not magnetic due to the incomplete vanadium oxide chain, while the $VO_2$ of the R phase at high temperature behaves as a paramagnetic metal under the magnetic field, so the magnetic susceptibility increases significantly when the temperature reaches the phase transition point (Berglund and Guggenheim, 1969).

The abrupt change in resistivity is one of the most obvious features of the $VO_2$ phase transition. When the temperature is lower than the phase change temperature, the resistivity of $VO_2$ is very large, about 1~10 Ω·cm, which is insulating or semiconductor, and when the temperature is higher than the phase change temperature, the resistivity decreases sharply, about $10^{-4}$~$10^{-3}$ Ω·cm, showing a metallic state. $VO_2$ will experience a 3-5 orders of magnitude resistance mutation at the phase transition point; the transition speed is fast, stable and reversible; and the phase transition temperature of the heating process and the cooling process is different, so there is a certain hysteresis phenomenon (Figures 6A, C).

## 3 $VO_2$ film preparation process

$VO_2$ does not undergo volume change during phase change as a thin film material (Kucharczyk and Niklewski, 1979; Béteille et al., 1999), So the film morphology is often used as the main morphology for $VO_2$ research and applications. So far, there are many preparation methods for $VO_2$ films, and different methods are suitable for different application fields.

Currently, the common methods include the sol-gel method (Bian et al., 2016; Chang et al., 2018; Danxia et al., 2015; Fallah Vostakola et al., 2019; Manning et al., 2005; Novodvorsky et al., 2015; Théry et al., 2016; Zou et al., 2019), the magnetron sputtering method (Chang et al., 2018), the vapour phase deposition method (Manning et al., 2005), the pulsed laser precipitation method (Novodvorsky et al., 2015), and so on (Bian et al., 2016; Théry et al., 2016). These test methods have some of the same drawbacks to a certain extent, such as high requirements for test equipment, complex process parameters, difficulty stabilising the control, poor process repeatability, and film properties. To make $VO_2$ films have a broader application prospect, future research work should focus on the following points: 1) optimise the $VO_2$ film preparation process.

Such methods as pulsed laser deposition, magnetron sputtering, and the sol-gel method can be used to obtain high-quality $VO_2$ films, but the appropriate choice of substrate and annealing process is the main factor affecting the performance of the prepared $VO_2$ films. Therefore, to prepare $VO_2$ films with excellent performance, the process parameters for preparing $VO_2$ films need to be continuously optimised. 2) Reduce the phase transition temperature of the $VO_2$ film. 68°C phase transition temperature to a certain extent limits the application of $VO_2$ film, due to most of the applications of $VO_2$ requiring its phase transition temperature to be close to room temperature, and doping is currently one of the most effective means to reduce the phase transition temperature of $VO_2$, so as far as possible, reduce the phase transition temperature of $VO_2$ and make the doped $VO_2$ film have optical and electrical properties to meet the requirements of the application of the future research focus. Therefore, minimizing the phase transition temperature of $VO_2$ and making the optical and electrical properties of the doped $VO_2$ films meet the requirements of applications are the focus of future research. 3) preparation of composite multilayer $VO_2$ film structures to enhance the phase transition properties and improve the magnitude of changes in electrical and optical properties before and after the phase transition. Some studies have shown (Zhou et al., 2013) that optimizing the optical design of $TiO_2/VO_2$ bilayer film and preparing a $TiO_2$ minus emission layer with a thickness of one-quarter wavelength can appropriately improve the transmittance and switching efficiency, but the study failed to address how to maintain high transmittance and switching efficiency while controlling the temperature of the phase transition. To obtain $VO_2$ films with the desired properties, this requires more in-depth theoretical studies and technical exploration by researchers.

## 3.1 Pulsed laser deposition (PLD)

Pulsed laser deposition is a typical physical deposition coating process, as shown in Figure 7C, in which a pulsed laser emits a high-energy beam onto a target until it reaches a molten state, and then the target is jetted onto a sinking bottom to form the desired thin film, typically vanadium, $VO_2$, or $V_2O_5$. The deposition atmosphere is generally oxygen or oxygen-argon mixed gas, and adjusting the partial pressure of oxygen can deposit vanadium oxide films with different oxygen contents, including vanadium dioxide.

The advantage of this process is that the composition is easy to control and can prepare thin films with complex components. In 1993, M. Borek et al. (1993) attempted to deposit $VO_2$ thin films using metal vanadium targets and introduced a mixture of argon and

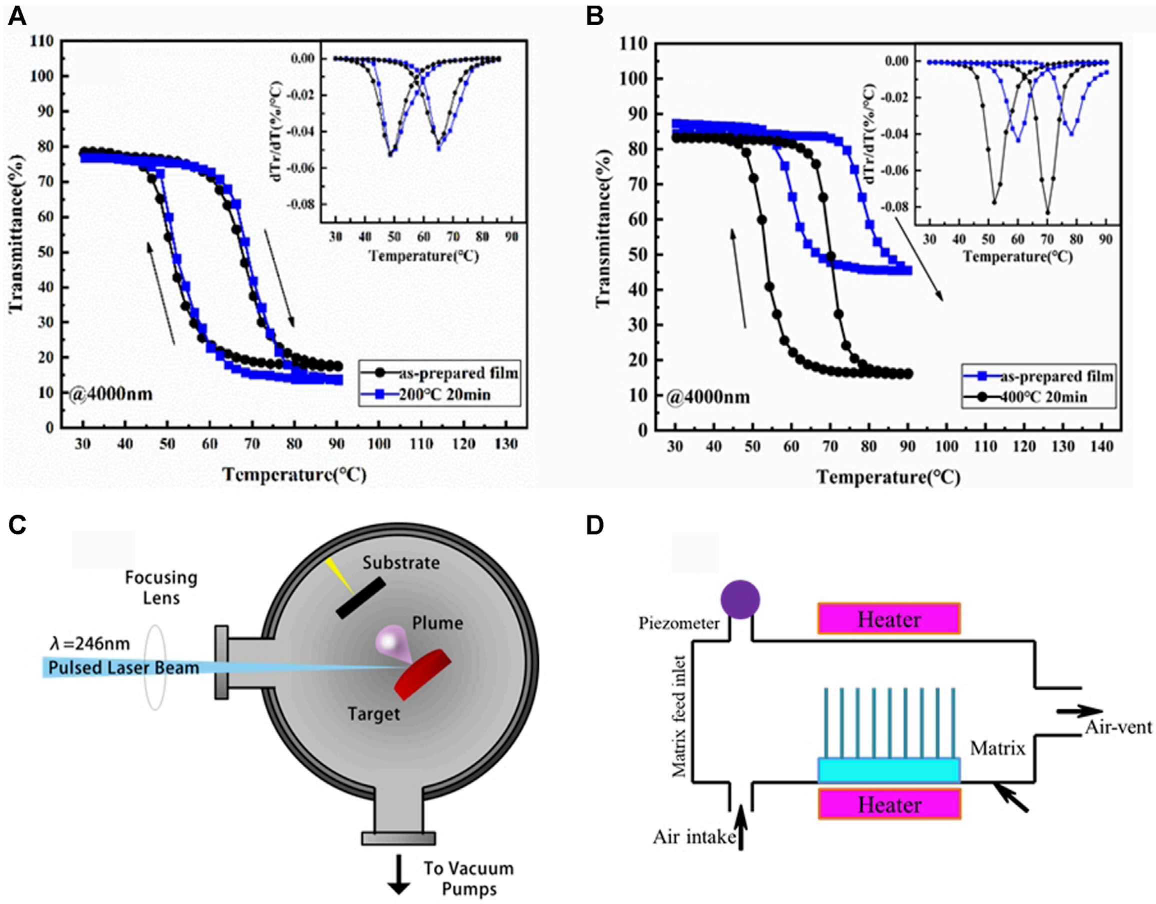


FIGURE 7
**(A,B)** Optical and Electrical Properties of $VO_2$ Thin Films (D. Li et al., 2015); **(C)** Schematic diagram of pulse laser deposition system; **(D)** Schematic diagram of CVD system.

oxygen. A $VO_2$ thin film with a significant phase transition effect was obtained at a substrate temperature of 500°C, and it was found that oxygen partial pressure has a significant impact on the valence state of the final product. Sayid Bukhari et al. (2020) investigated the effect of oxygen flow rate on the phase transition characteristics of $VO_2$ thin films deposited on amorphous thermal oxide ($Si/SiO_2$) substrates by the PLD method, suggesting that oxygen diffusion may play a crucial role due to flow rate.

The thin film prepared by this method can also be doped with other elements, and the deposition speed is fast and pollution-free, with good crystal quality and a flat surface. M. Soltani et al. (2004) used PLD to deposit W-doped $VO_2$ films and W- and Ti-doped $VO_2$ films on quartz surfaces, respectively. Research has found that the infrared transmittance of $V_{1-x-y}W_xTi_yO_2$ thin film is significantly higher than that of $V_{1-x}W_xO_2$ thin film. W doping can effectively reduce the phase transition temperature point of $VO_2$ thin film, and the introduction of Ti can reduce the width of the thermal loop and increase the resistance temperature coefficient. However, this method also has obvious drawbacks. When laser bombardment occurs, particle aggregates are formed, and their composition uniformity can only be maintained within a small area; therefore, the deposited thin film can only be obtained on a very small substrate and cannot be prepared on a large area.

## 3.2 Magnetron sputtering method

The sputtering method is the most common and direct method for preparing $VO_2$ thin films, and the general sputtering device will be attached to a magnetic field, so this preparation process combining magnetron technology and bipolar sputtering technology is called the magnetron sputtering method. It belongs to the physical vapor deposition process. During sputtering, the V-containing particles are continuously emitted to the rotating substrate, and these particles collide with the substrate surface or other particles, some of which are reflected and consumed, and the other part stays on the surface. The trapped particles then undergo surface diffusion and migration, some of which evaporate again and some of which fall into the bottom of the potential energy and are adsorbed by the surface; that is, the condensation process occurs. The condensation process is generally the generation and continuous growth of island particles, that is, the formation and growth of crystal nuclei, and finally the formation of a continuous film (Z. Zhang and Lagally, 1997). Its advantages are that the deposition rate of the film is relatively fast, the composition is easy to control, the film adhesion ability is strong, and the sequential multi-layer preparation of the composite film can be realized. According to the difference in the power supply used in sputtering equipment, it can be divided into RF magnetron sputtering, ion beam sputtering, and DC magnetron sputtering.

Magnetron sputtering has the advantages of high adhesion and easy control of film thickness, but the common problem is that the film has low purity and often contains vanadium oxides in other valence states. The presence of these substances affects the phase transition temperature and its characteristics. The study of preparing $VO_2$ films by magnetron sputtering began after 1970 (Babulanam et al., 1987), it has been widely adopted to this day and has undergone extensive research by scholars during this period. Xu Guo et al. (G. Xu et al., 2005) used radiofrequency reactive magnetron sputtering to the epitaxial growth of $VO_2$ thin films on α-AlO (0001) substrate was studied to investigate the effect of 3–150 nm film thickness on optical properties. The results showed that as the film thickness decreased, the crystal metal phase transition temperature of $VO_2$ thin films significantly decreased. The regulation of MIT phase transition temperature is also of great significance in the preparation of $VO_2$ thin films. Jiang Meng et al. (M. Jiang et al., 2014) successfully synthesized $VO_2$ thin films with various oxygen flow ratios on quartz glass through reactive magnetron sputtering. They found that by accurately adjusting the oxygen flow ratio without doping elements, the phase transition temperature can be controlled between 46°C and 72°C. Compared with traditional magnetron sputtering technology, it can deposit high-quality thin films, and the $VO_2$ thin films deposited using this method have excellent performance.

Compared with traditional RF magnetron sputtering, the $VO_2$ thin film prepared by HiPIMS technology is denser, smoother, and has strong anti-aging performance. As Dou et al. (2021) found, the thermochromic ability of $VO_2$ can be optimized by adjusting the average power of HiPIMS, and $VO_2$ deposited on polished aluminum foil can change its infrared emissivity at different temperatures, making it an ideal choice for infrared signals and detection in many industrial and military applications.

$VO_2$ generated by sputtering is not very pure and often contains other oxides of vanadium, such as $V_2O_5$, $V_2O_3$, VO, etc. The presence of these oxides affects the phase transition properties. The presence of these oxides affects the nature of the phase transition. To improve the purity of $VO_2$, annealing, and laser sintering can be used to control the process conditions. Annealing is at 450°C temperature in the $N_2$ gas stream holding 2–10 h, and sintering is at 350°C with a ruby laser emitted by the 0.6943 μm laser on the membrane layer to irradiate the beam energy of a few joules per square centimeter of irradiation period of 2 ms. Annealing or laser sintering can greatly increase the temperature-phase transition of the conductivity and the amplitude of the jump. The larger the jump, the higher the purity of the $VO_2$ component. Geng Chen (Geng et al., 2022) prepared surface nanoparticle thin films by combining HiPIMS with annealing post-treatment. The particle size of the surface nanoparticle can be adjusted by controlling the oxygen flow rate. However, there is currently a lack of detailed research on the film formation mechanism during high-energy pulse magnetron sputtering deposition.

## 3.3 Sol-gel method

The sol-gel method is a commonly used chemical preparation method for the preparation of $VO_2$ films. Compared with other preparation processes, the equipment used in this process is simple, and because of the use of sol instead of powder, the product has high uniform purity, easy stoichiometry, and can be applied to the preparation of large-area films, so it is widely used. The sol-gel method can be divided into two categories according to the different formation processes: the inorganic sol-gel method and the organic sol-gel method, both of which can be used to prepare $VO_2$ films with excellent performance.

In 1996, Lu et al. (1997) successfully prepared $VO_2$ films using the organosol-gel method and explained that the phase transition of $VO_2$ materials is the transition from monoclinic to tetragonal rutile by coordination field theory. Li et al. (2015) prepared $VO_2$ films on muscovite substrates using the inorganic sol-gel method, and investigated the thermal stability of the films by changing the annealing temperature and annealing time. The crystal structure and morphology of the films before and after annealing were studied by X-ray diffraction and other equipment (Figures 7A, B), and the $VO_2$ films were quite stable at an annealing temperature of 200°C, while when the annealing temperature reached 400°C, the phase transformation temperature of the $VO_2$ films would rise, and the $VO_2$ would gradually oxidize to $V_2O_5$, resulting in a decrease in the phase transformation efficiency of the $VO_2$ films. The organosol-gel method can also be doped with other ions to improve its characteristics. Chae et al. (2008) prepared W-doped and Ti-doped films using an organosol-gel method, respectively, and combined with a simplified annealing process, the films containing 12% W atoms doped showed a decrease in the phase resistance of the insulator, while the 20% Ti atom-doped films showed a smaller change in resistance at the phase transition temperature. In the future, the organosol-gel method needs to be further studied in the selection of doped ions so that the phase change temperature is more suitable for the application and cheaper raw materials can be found to reduce the cost.

For both inorganic and organic methods, the process should be improved to reduce the preparation cycle and improve efficiency. For example, the process of melting raw materials can be combined with electromagnetic technology to improve the melting efficiency. The selection of substrate is also very important; the appropriate substrate will make the film more uniform, more adhesion, and more dense, so in addition to the commonly used mica and silicon wafers, we should also find more excellent materials.

## 3.4 Chemical vapor deposition (CVD)

Chemical vapor deposition is a traditional technology for preparing thin films, the principle of which is to use gaseous precursor reactants to decompose certain components in the gaseous precursor through atomic and molecular chemical reactions and form thin films or other crystals on the matrix substrate. A schematic diagram of the chemical vapor deposition method is shown (Figure 7D). The preparation of $VO_2$ films from CVD was first reported in 1966, and this method has since been greatly popularized. At present, the vanadium sources for the preparation of $VO_2$ films by CVD method are mainly various metal-organic compounds, such as V $(acac)_3$, $VO(acac)_2$, and $VO(OC_3H_7)_3$ (Binions et al., 2007a; Binions et al., 2007b; Piccirillo et al., 2007). The process of preparing $VO_2$ films from CVD generally requires the deposition of vanadium oxides (such as $V_2O_5$) and then the reduction to +4-valent $VO_2$ films in a reducing atmosphere. This method is widely used in the development of new crystals, the purification of substances, and the deposition of various monocrystalline and polycrystalline thin film materials.

The raw materials used in this method are relatively inexpensive and do not require vacuum equipment, so the cost is low, while the deposition efficiency is very high and the product quality is very stable. At the same time, the disadvantages of the CVD method are also very obvious. The film preparation process is complex, and the structure and growth form of the film are strongly affected by the substrate temperature, reaction gas composition, gas flow rate, and other factors that are difficult to control, so it is not conducive to large-area preparation. Vernardou et al. (Vernardou et al., 2011) used atmospheric pressure vapor deposition to prepare thin films on glass substrates and found that the purity and structural properties of vanadium dioxide were affected by the solution ratio. Sahana et al. (Sahana et al., 2002) used diacetylacetone oxide vanadium oxide as a raw material to prepare thin films with glass as substrate by the low-pressure vapor deposition method and determined the temperature range (748~793 K) with the highest purity of vanadium dioxide deposited.

The current development trend is to change the phase transition temperature defects. This is due to the fact that different materials have different evaporation rates, so it is not easy to control the proportion of components. Manning et al. (2004) used $VCl_4$ as a raw material to fully study the CVD method for the preparation of $VO_2$ films and successfully doped $VO_2$ films with a variety of elements (W, Ti, Mo, and Nb). They considered that the appropriate doping elements could effectively reduce the phase transition temperature of the film, and the phase transition temperature of the film gradually decreased with the increase in doping amount.

## 3.5 Other preparation processes

In addition to the above commonly used preparation methods, there are the hydrothermal method, thermal decomposition, hydrogen-water balance method, evaporation method, etc. But there are limitations: it is not easy to achieve industrial production; the film obtained by the evaporation method has poor compactness and low adhesion; the hydrogen-water balance method is still in the laboratory stage; and it needs to be improved in order to achieve industrialization. It is also necessary to find new preparation processes to prepare films with different characteristics to meet different needs.

# 4 Regulation of $VO_2$ film properties

$VO_2$ flexible film is a specific film based on the thermochromic performance of $VO_2$ nanoparticles, which can actively adjust its own optical transmittance at different external temperatures. The layered structure is the basic property of $VO_2$ films, and light hitting different layers of the film is divided into two parts: reflection and transmission. According to the Maxwell-Garnett effective medium theory (EMT), adjusting the size of nanoparticles in layered coatings can obtain effective dielectric functions with different values, which in turn affect their transmittance and reflectivity (Laaksonen et al., 2014).

There are a number of ways to change the phase transition temperature of vanadium dioxide films, such as doping, stress, particle size, non-chemical stoichiometry, microstructure, etc. Of these, doping is considered to be the most direct, effective, and practical for application. Among them, doping is considered to be the most direct, effective, and practicable method of application. Jorgenson and Lee (1986) proposed as early as 1986 the direct preparation of ion-doped $VO_2$ thin films ($V_{1-x}M_xO_2$) by sputtering, where M denotes the doped ions. Until now, there have been many reports on doped $VO_2$ films. In addition to doping elements to enhance both visible light transmittance and solar modulation, methods such as preparing porous materials (Zhou et al., 2013; Cao et al., 2014a), compositing vanadium dioxide with other functional materials to form core-shell structures (Gao et al., 2012; Li et al., 2013), and heterostructures (Chen et al., 2004; Zhou et al., 2014) are also able to take into account both of the above-mentioned performance enhancements. While it is one of the ultimate goals of researchers to apply $VO_2$ films on a large scale for energy-saving applications, the dimming ability of $VO_2$ films needs to be further improved, and multilayer compositing of $VO_2$ films has been considered the most promising process to improve the overall performance of the products. Surface structure also has an impact on the performance of $VO_2$ films, in which the use of printing can achieve large-scale, high-volume production of $VO_2$ films, which is conducive to expanding the application of $VO_2$ films in the intelligence of cold chain packaging systems. In this section, we summarise the existing domestic and international research explorations on the regulation of $VO_2$ film properties, starting from the visible light transmittance and solar energy regulation, phase transition temperature, weathering resistance, large-scale coating, and other application performance indexes of vanadium dioxide films.

## 4.1 Effect of elemental doping on the properties of $VO_2$ films

### 4.1.1 Effect of single element doping on the properties of $VO_2$ films

Doping is one of the most effective ways to reduce the phase transition temperature of $VO_2$ films (Table 1), and the doping of $Mg^{2+}$, $Al^{3+}$, $Ti^{4+}$, $Tb^{3+}$, $Mo^{6+}$, $W^{6+}$, and $F^-$ can play a role in reducing Tc (Chen et al., 2017). So far, $W^{6+}$ is the most effective dopant for reducing Tc among all elements, and every 1% of the number of W atoms doped can reduce Tc by about 20~26°C (Chen et al., 2015).

Chen et al. (2017) suggested that this is due to the change in the electronic structure of $VO_2$ due to W doping. For $W_xV_{1-x}O_2$ films, $W^{6+}$ enters the $VO_2$ lattice and replaces $V^{4+}$, breaks the $V^{4+}$—$V^{4+}$ covalent bond and reconstructs $V^{3+}$—$W^{6+}$ along the axis of $VO_2$(M), and the two electrons in the d orbital of the W ion combine with the adjacent $V^{3+}$—$V^{4+}$ along the $VO_2$(M) axis to compensate for the loss of the $V^{4+}$—$V^{4+}$ covalent bond. Therefore, the phase transition temperature of the low-temperature semiconductor $VO_2$(M) is very unstable, the energy level of the dII. orbital and the $O^{2p}$ orbital decreases, and the relative orbital position of the π* and dII. orbitals shifts, which indicates that the occupancy of the $d_{II}$. orbital decreases and also means that the intensity of the V—V bond interaction decreases. This will cause the Fermi level guide band to move and reduce the band gap, so Tc decreases and $VO_2$ has distinct metallic properties. The same theoretical principle applies to the doping of other metals.

Wang et al. (2016) first reported the incorporation of terbium cation ($Tb^{3+}$) into $VO_2$ films to reduce Tc and increase Tlum. When the doped atomic fraction was 2%, the Tlum and $\Delta T_{sol}$ of the film increased from 45.8% to 7.7%–54.0% and 8.3%, respectively.

TABLE 1 Effects of different doping elements on the properties of $VO_2$ films.

| Alloying element | Doped atomic number fraction x/% | Film color | $T_{lum}$/% | $\Delta T_{sol}$/% | $\frac{dT_c}{dx}$ | References |
|---|---|---|---|---|---|---|
| Mg | 5.0 | Bronze | 82.1 | 4.8 | −3.0 | Wang et al. (2015b) |
| Tb | 2.0 | | 54.0 | 8.3 | −1.5 | Wang et al. (2016a) |
| Al | 8.0 | Brown | 46.5 | 7.6 | −1.3 | Ji et al. (2018c) |
| Ti | 1.1 | Brown | 53.0 | 17.2 | | Chen et al. (2013) |
| Eu | 4.0 | Bronze | 54.0 | 6.7 | −6.5 | Cao et al. (2014b) |
| Mo | 11.0 | | 45.0 | 25.0 | −12.0 | Batista et al. (2011) |
| Zr | 8.5 | Pale yellow | 55.1 | 14.6 | −0.3 | Long et al. (2018) |
| W | 2.0 | Fulvid | 45.1 | 6.9 | −20.0 | Hu et al. (2016) |
| F | 2.9 | Fulvid | 48.7 | 10.7 | −11.3 | Dai et al. (2013) |
| W + Zr | 0.6/8.5 | Pale yellow | 56.4 | 12.3 | −1.3 | Shen et al. (2014) |
| W + Sr | 11.9/0.9 | Misty gray | 61.4 | 5.2 | −3.0 | Dietrich et al. (2017) |
| W + Mg | 2.0/4.0 | Bronze | 81.3 | 4.3 | −5.5 | Wang et al. (2015a) |

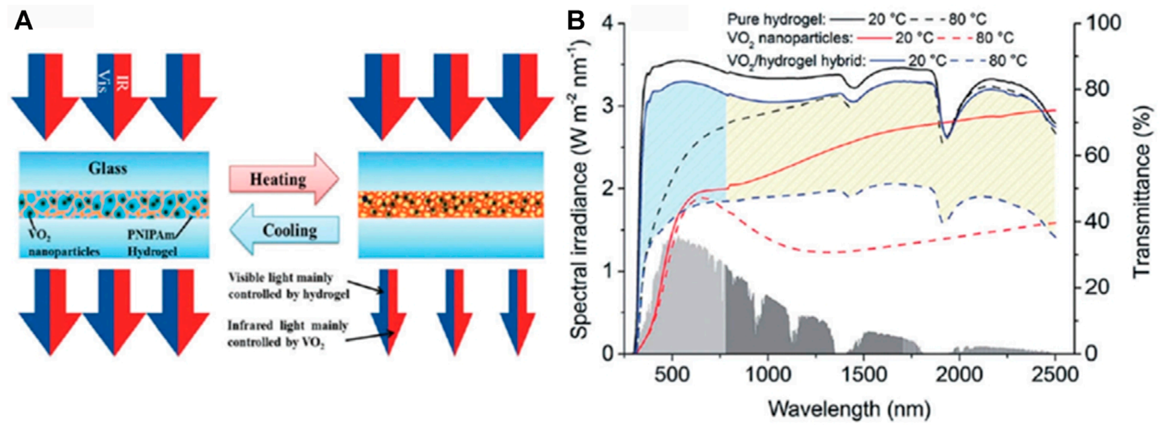


FIGURE 8
$VO_2$/PNIPAm: **(A)** Solar light regulation mechanism; **(B)** UV-Vis NIR spectra (Zhou et al., 2014).

Moreover, when the atomic number fraction of $Tb^{3+}$ reaches 6%, the Tlum of the film can be as high as 79.4%.

Single-element doping, in some cases, does not always produce good results, For example, single Mg doping can improve the optical properties of the film, but it is not conducive to the reduction of Tc, which hinders the application range of $VO_2$ film.

### 4.1.2 Effect of multi-element co-doping on the properties of $VO_2$ films

It has been found that the use of co-doping is used to make $VO_2$. Modification can effectively reduce the adverse consequences of single-element doping TC and, at the same time, further adjust its optical performance.M. K. Dietrich et al. (Dietrich et al., 2017) prepared a tungsten-strontium (Sr) co-doped $VO_2$ film, in which, with the increase in the doping amount of Sr (atomic radius of 215.1 p.m.), the atomic overlapping orbitals will decrease correspondingly, thereby increasing the band gap, and the film will gradually appear grayish-white. When the doped atomic fractions of Sr and W were 11.9% and 0.9%, respectively, the Tlum of the film reached 61.4%. In addition, the researchers also targeted W-F (Burkhardt et al., 2002), W-Mg (Wang et al., 2015a) and W-Al (Yanase et al., 2018). The plasma combination was used to explore the direction of co-doping.

In summary, it can be seen that the phase transition temperature of $VO_2$ can be controlled by chemical element doping while maintaining the optical properties of $VO_2$. Table 1 shows the effects of different doping elements on the properties of $VO_2$ films. The main elements commonly used in doping $VO_2$ materials to reduce their phase transition temperature are $W^{6+}$, $Mo^{6+}$, etc., which can change the energy level structure of $V^{4+}$, and they are comparable to the ionic radius of $V^{4+}$, which can avoid the destruction of $VO_2$ crystal structure.

## 4.2 Effect of composite microstructure on the properties of $VO_2$ thin films

Core-shell structures have received increasing attention due to their replaceable components and modifying effects. $VO_2$-based core-shell structures can obtain more properties, such as $SiO_2$ shells, which can significantly enhance the antioxidant and optical properties of $VO_2$ nanoparticles, etc. Gao et al. (2012) prepared a stable and transparent $SiO_2/VO_2$ core-shell structure. It has UV-shielding properties and an obvious temperature-responsive thermochromic phenomenon in the near-infrared region. Another $VO_2$(M)@$SiO_2$ nanofiber structure prepared by a one-step hydrothermal method (Li et al., 2013) can have a visible light transmittance of more than 50%. This is the result of the combined effect of a smaller fibre radius and a narrower light-acting space.

In addition to the core-shell structure, the hybrid structure is also an effective way to improve the thermochromic properties of vanadium dioxide. Chen et al. (2004) prepared a nano-$VO_2$-$SiO_2$ monolayer hybrid membrane with high visible light transmittance using the sol-gel method. In the membrane, the presence of $SiO_2$ increased the visible light transmittance without sacrificing other properties of the membrane. The $VO_2$-$SiO_2$ monolayers with a Si/V ratio of 0.05 showed up to 75% transmittance at 700 nm compared to the normal $VO_2$ films. Zhou et al. (2014) reported $VO_2$ hydrogel hybrid films with ultrahigh optical properties, as shown in Figure 8. Combining inorganic $VO_2$ with organic thermochromic materials, they found that the introduction of poly N-isopropylacrylamide (PNIPAm) significantly increased the $\Delta T_{sol}$ to 25.5% while maintaining 70.7% $T_{lum}$. The reason for this dramatic improvement in performance is that $VO_2$ and PNIPAm hydrogels exhibit different visible transmittance and solar modulation at low and high temperatures. $VO_2$ exhibits low $T_{lum}$ and high $T_{sol}$, while PNIPAm exhibits high $T_{lum}$ and low $T_{sol}$, and the coupling of the two results in a balance of $T_{lum}$ and $T_{sol}$.

## 4.3 Effect of multi-coat composite on $VO_2$ films

### 4.3.1 $VO_2$ double-layer film composite

$VO_2$ bilayer film is a double-layer film made by compounding unmodified $VO_2$ film with other functional films by coating, embedding, or deposition, thereby improving the optical properties

TABLE 2 Comparison of optical properties of different layered $VO_2$ films.

| Laminated structure | Thickness/nm | $T_{lum}$/% | | $T_{sol}$/% | | References |
|---|---|---|---|---|---|---|
| | | *L* | *H* | *L* | *H* | |
| $VO_2/TiN$ | 130 | 49.0 | 51.0 | | | Hao et al. (2018) |
| $VO_2/VO_3$ | 120 | 25.2 | 22.7 | 30.2 | 17.0 | Long et al. (2018) |
| $V_2O_3/VO_2$ | 50 | 35.6 | 36.7 | 38.5 | 34.4 | Sun et al. (2016) |
| $VO_2/SiO_2$ | | 32.2 | 30.1 | 27.6 | 26.3 | Zhu et al. (2016) |
| $VO_2$/FTO | 65 | 34.0 | 28.6 | 4.9 | | Zhang et al. (2011) |
| $WO_3/VO_2/WO_3$ | 110 | 55.4 | 53.9 | 47.2 | 42.9 | Long et al. (2016) |
| $ITO/VO_2/TiO_2$ | 290 | 56.1 | | | | Miller and Wang (2016) |
| $TiO_2(R)/VO_2/TiO_2(A)$ | 440 | 30.1 | 27.8 | 33.8 | 23.9 | Zheng et al. (2015) |
| $VO_2/SiO_2/TiO_2$ | 5,000 | 17.8 | 18.2 | 28.8 | 13.6 | Powell et al. (2016) |
| $TiO_2/VO_2/TiO_2/VO_2/SiO_2/TiO_2$ | 490 | 45.0 | 42.3 | 52.1 | 40.0 | Mlyuka et al. (2009) |

of $VO_2$ film. Hao Q et al. (Hao et al., 2018) embedded a TiN plasmonic nanoarray with a hexagonal superlattice structure between the substrate and the $VO_2$ film and relied on the good absorption performance of TiN for near-infrared (NIR) light to create a local heating phenomenon to promote the phase transition rate of the $VO_2$ film. Based on this, $VO_2$/TiN composite films can be prepared that can sensitively respond to changes in external temperature and light intensity. The smart coating blocks direct infrared light at 28°C and transmits infrared light at low light intensity or below 20°C. In addition, the film is capable of achieving a Tlum of 51% and an infrared conversion efficiency of 48% at 2000 nm. However, this method requires nitriding of titanium oxide at 850°C for 10 h and subsequent annealing of the composite film, which is complex and requires high energy consumption.

The refractive index of $VO_2$ films is different before and after the phase transition (n ($VO_2$(M)) = 2.7~2.8, n ($VO_2$(R)) = 2.0~2.5), and all of them are greater than the refractive index of air ($n^{air}$ = 1) (Li et al, 2013), resulting in a higher reflectivity of the $VO_2$ film when exposed to sunlight, which reduces the optical performance of the $VO_2$ film. Antireflective structure (ARS) is a functional structure of thin film materials that can further reflect the light refracted in the film to reduce the loss of light and has a better anti-reflection effect on the surface of the film when it is lower or higher than the phase change temperature.

### 4.3.2 $VO_2$ multilayer film (number of layers≥3) lamination

On the basis of the $VO_2$ bilayer film, the researchers have conducted in-depth research on multilayer $VO_2$ films with a number of n ≥ 3 layers, which can not only further reduce the loss of light to enhance the transmittance of the film but also expand the application range of $VO_2$ multilayer films according to the characteristics of different functional layers. Studies have shown that the $T_{lum}$ of a three-layer $VO_2$ film can reach up to 86%, while the five-layer structure can achieve a $\Delta T_{sol}$ increase of about 12% (Liu et al., 2013). Mlyuka et al. (2009) prepared a five-layer hybrid film of $TiO_2/VO_2/TiO_2/TiO_2$ by magnetron sputtering by using a $TiO_2$ layer with high light transmittance and anti-reaction effect and two layers of $VO_2$ thermochromic layer, and the hybrid film had high $T_{lum}$ and $\Delta T_{sol}$ ($T_{lum}$ = 45%, $\Delta T_{sol}$ = 12.1%).

In summary, the multi-coating structure design of $VO_2$ films has been regarded as the most promising means to improve the comprehensive properties of thin films. Table 2 shows a comparison of the optical properties of different layered $VO_2$ films, among which there are few reports on the structure of more than three layers, which may be due to the fact that the synthesis process of $VO_2$ films is not easy to control and the preparation process of multilayer films is complex. Although the multi-layer coating structure of $VO_2$ film is mainly to improve the practical performance of $VO_2$ film itself, such as dimming ability, phase change temperature, durability, etc., there is also room for the development of multi-layer film structure design. For example, based on the performance of the composite layer, it can be multi-functional (self-cleaning, anti-fogging, scratch resistance, etc.) at the same time to meet the diverse needs of $VO_2$ film materials in the use process.

## 4.4 Effect of surface structure on $VO_2$ films

### 4.4.1 $VO_2$ nanoparticle films

When light comes into contact with the surface structure of nanoparticles or thin films, different degrees of transmission and reflection occur. Core-shell nanocomposites composed of $VO_2$ nanoparticles and highly transparent metal oxides such as $TiO_2$ have emerged as a new material to enhance visible light transmittance (Wang et al, 2016). On the one hand, the highly transparent metal oxide housing material does not block the ingress of light, and at the same time, it can use its anti-reaction effect to reduce light loss and improve the optical properties of $VO_2$ films. On the other hand, the housing material can prevent $O_2$ or acid erosion and enhance the chemical stability of $VO_2$ nanoparticles.

Ji et al. (2019) synthesized novel $VO_2$/ZnS core-shell nanoparticles (Ji et al., 2018a) using thioglycolic acid as ligand, and used them as raw materials to prepare inks. The $VO_2$ film prepared by inkjet printing technology based on infrared transparent nano-polyethylene has good infrared thermochromic performance, and the $\Delta T_{sol}$ is 32.4% at a fixed wavelength of 20.0 μm. In addition, a 560 $cm^2$ large-size $VO_2$ nanoparticle film with good homogeneity was successfully fabricated. This is conducive to expanding the application of $VO_2$ flexible thermal insulation and temperature control film in cold chain packaging systems and realizing the research and development of large-capacity $VO_2$ thermochromic intelligent incubators, thereby helping to save cold chain logistics and transportation costs.

#### 4.4.2 $VO_2$ film surface patterning

In addition to the surface modification of nanoparticles, the design of patterned structures on the surface of thin films is also one of the research hotspots. Cao et al. (2017) prepared a single layer of dense polystyrene (PS) spheres on a fluorine-doped $SnO_2$ conductive glass $SnO_2$:F (FTO) substrate using a gas-liquid interface self-assembly method, followed by a mixture of $SiO_2$ and different amounts of $VOC_2O_4$ and spin-coating directly between the PS balls, and finally toluene to remove the monolayer of PS balls. The prepared smooth film is converted into $VO_2/SiO_2$ film by a rapid thermal annealing process in a nitrogen atmosphere. The ordered $VO_2/SiO_2$ composite film has good thermochromic properties with a $\Delta T_{sol}$ of 8.42% and an increase in Tlum to 55.6%.

Lu et al. (2016) used screen printing to prepare $VO_2$ films with periodic and micropatterned structures. Such a network structure can enhance visible light transmittance (Tlum = 21.4%) compared to conventional continuous nanocomposite films. Due to the openness of the grid, $VO_2$ films with a thickness of 1,000 μm can be prepared, so the $\Delta T_{sol}$ increases with the $VO_2$ powder content. Compared with the theoretical results of the lattice structure films, the experimentally measured $\Delta T_{sol}$ is as high as 17.2%, which exceeds the calculated value of $\Delta T_{sol}$ = 16.5%.

In general, the surface structure of $VO_2$ films can be adjusted by designing the patterned structure of nanoparticles and film surfaces, the optical properties of the prepared $VO_2$ films can be improved, and the chemical stability of the films can be enhanced.

## 5 Research on the application of $VO_2$ film

The vanadium dioxide phase transition is usually achieved in thermally induced phase transformation, electrolytically induced phase transformation and photoinduced phase transformation, and the optical properties before and after the phase transformation are abruptly changed (Li et al., 2017; Taylor et al., 2013). Based on this characteristic, vanadium dioxide is widely used in smart windows, optical switches, terahertz modulators, optical storage materials, transistors and other fields. This article lists some popular applications of vanadium dioxide.

### 5.1 Thermochromic smart windows

Building energy consumption is an important aspect of the total energy consumption of society, accounting for about one-third of it. Windows are the least energy-efficient part of a building due to their extremely low efficiency, and their energy consumption accounts for a large part of the building's energy consumption (Xu et al., 2018). As the demand for architectural glass surges, so does the demand for thermal insulation, so the application of smart glass is becoming more and more extensive. The thermochromic coating has high transparency for the incident indoor light at low temperatures and high reflection for the light in the incident room at high temperatures, so it can intelligently adjust the indoor temperature and reduce heating and cooling energy consumption in the building (Wu et al, 2013). As a special phase change material, vanadium dioxide film has a phase change temperature of 68°C, which can undergo SMT transformation according to the change in temperature. Before and after the phase transition, it has very different optical properties. For example, the transmittance of visible light to infrared light changes from high transmission to high reflection, but this does not happen before or after the phase transition. The monoclinic to rutile phase transition of vanadium dioxide is accompanied by a sudden change in optical properties and even reaches a modulation amplitude of 80% in the near-infrared region (Chen et al., 2019). This excellent thermochromic property makes vanadium dioxide a popular material for designing smart windows. In fact, there have been a lot of reports on the application of $VO_2$ in the direction of smart windows. However, there are still several difficulties in the application of vanadium dioxide in the direction of smart windows: 1) The phase change temperature is adjusted to near room temperature; 2) The environmental stability of $VO_2$ thin film coatings is altered; and 3) Improve visible light transmittance; 4) Improve the ability to regulate solar energy (Zhang et al, 2020). This necessitates the modification of the smart window to improve its performance by improving the visible light transmittance and solar energy modulation amplitude.

For example, WU et al. from Wuhan University of Technology successfully prepared a microporous vanadium dioxide film using cotton as a template (Wu et al., 2018). By changing the temperature of the hydrothermal reaction, the micropore size and the grain size of vanadium dioxide can be adjusted, and when the hydrothermal reaction reaches 180°C, the grain size of vanadium dioxide is 60.7 nm, and the modulation amplitude of sunlight is maintained at 12.9%. Other than that, Qian et al. have taken a unique approach by borrowing from a biomimetic structure (Figure 9A), where vanadium dioxide is deposited in the imitation moth eye on the nano-silica structure (Qian et al., 2014). When the size of a single moth-like eye reaches 21 nm, the visible light transmittance and sunlight energy modulation amplitudes of the film reach 44.5% and 7.1%. Most important of all, the thin film simulations show that this structure might be able to reach a 70% pass rate and a 15.5% sunlight energy modulation amplitude (Figure 9B).

In order to solve the problem that the $T_C$ of $VO_2$ films is too high and the $T_{lum}$ is too small, the researchers studied the thermochromic properties of elemental doping. As a thermochromic coating material, the $T_C$ of $VO_2$ film should ideally be reduced to around room temperature (25°C). Doping includes single-element doping and multi-element doping. Among the two doping methods, the

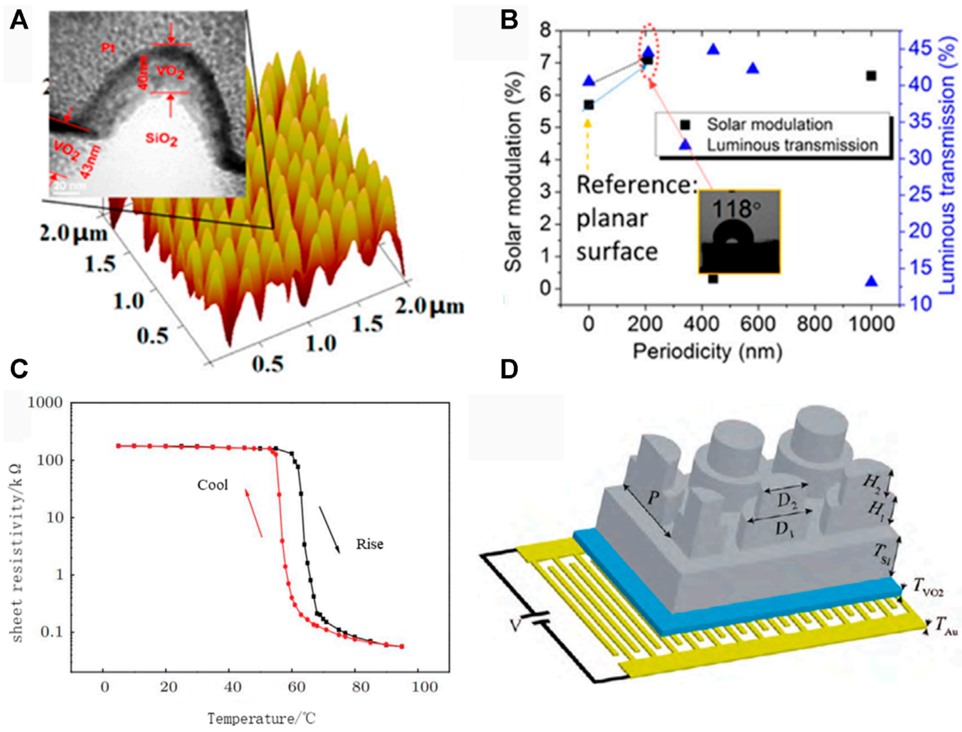


FIGURE 9
**(A)** Moth-like eye structure vanadium dioxide and its; **(B)** thermochromic properties (Qian et al., 2014); **(C)** the temperature of the vanadium dioxide film-Resistance change curve (Reese et al., 2004); **(D)** Broadband THz switch schematic (Schalch et al., 2020).

study of single-element doping is more extensive and in-depth. Among the many doped elements, W has the best effect on reducing the $T_C$ of $VO_2$ nanoparticles. Li et al. prepared mesoporous tungsten oxide nanocrystals doped with tungsten (W) by hydrothermal method (Li et al., 2019). By adjusting the doping amount of W, the phase transition temperature of $VO_2$ changes inversely. With the increase in W content, $T_C$ decreased significantly and $\Delta T_{sol}$ increased significantly. The paper increases the content of W from 0.2 at% to 0.6 at% and reduces the phase transition temperature of $VO_2$ from 56.9°C to 39.5°C. Compared with the undoped $VO_2$, the phase transition temperature ($T_C$ = 39.5°C) of the 0.6 at% doped $VO_2$ film is very close to room temperature, which is conducive to practical application. Zhang et al. prepared pure w-doped thin films (20–50 nm) by a simple hydrothermal recrystallization method. In the range of 0–1.1 at%, the phase transition temperature of W-doped $VO_2$ decreases with the increase in W doping amount, which is 28.4°C/W. In addition, nano-titanium dioxide films exhibit excellent thermochromic properties at 42.7°C for $T_C$, 61.7% for $T_{lum,}$ and 11.7% for $\Delta T_{sol}$ (Zhang et al., 2020). The doping of the W element achieves the effect of reducing $T_C$ at the expense of tum and $\Delta T_{sol}$. Unfortunately, high-valent doping, similar to W-doping, also significantly reduces the optical properties of $VO_2$ films. Since most single-element doping can only partially alter thermochromic properties, multi-element doping is used to improve overall performance. Doping W is the most effective way to reduce the phase transition temperature. W is mixed with cations that have lower equivalent states for magnesium (Mg), strontium (Sr), rare earths, and aluminium (Al) compared to $V^{4+}$. This shows that W can improve $T_{lum}$. Guo et al. synthesised W-Zr-doped $VO_2$ by a feasible hydrothermal method, and the appropriate W-doping level significantly reduced $T_C$ (Guo et al., 2021). The incorporation of Zr significantly increased the $T_{lum}$ and $\Delta T_{sol}$ values of $VO_2$. The addition of W and Zr had a significant influence on the microstructure properties of the $VO_2$ film, with samples of $V_{0.95}$ $W_{0.01}$ $Zr_{0.040}$ $O_2$ and $V_{0.94}$ $W_{0.02}$ $Zr_{0.04}$ $O_2$ showing the purple and flower-shaped shapes, respectively. The $V_{0.95}$ $W_{0.01}$ $Zr_{0.040}$ $O_2$ film exhibited excellent thermochromic properties ($T_C$, $T_{lum}$ and ΔTsol) at 46.9°C, 60.7%, and 10.6%, respectively. In addition to the above-mentioned co-doping with W, the researchers also found that other elements of co-doping can improve $VO_2$ film performance. C. JI et al. used a co-doping strategy to lower the temperature at which the phases changed and keep the improved optical performance. After the $VO_2$ film was co-doped with Fe (9.2%) and Mg (3%), all the thermochromic parameters were enhanced on the glass substrate, among which the light transmittance was increased to 42.1%, the solar modulation ability was increased to 12.8%, and the phase change temperature was reduced to 38.2°C. Ji et al. (2018b) discovered that the co-dopant $Fe^{3+}/Mg^{2+}$ works together to stop the neutralization of $e^-$ and $h^+$ carriers. This creates a good balance between the temperature at which light passes through and the temperature at which the phase transition occurs (Ji et al., 2018c). In 2021, Y. Zhang et al. made a $ZnV_2O_7$-$VO_2$ composite film on a quartz substrate using a magnetron co-sputtering system. They added $Zn_2V_2O_7$ (Sameie et al., 2018) to make the sample more clear and bright by increasing the band gap from 1.7 eV for pure $VO_2$ to 2.8 eV for the composite $ZnV_2O_7$-$VO_2$, which caused a blue shift at the absorption edge and better light transmission (Zhang et al., 2021). The introduction of $Zn_2V_2O_7$ makes the composite film exhibit a better thermochromic performance value, with a light transmittance of 49.0%, a solar modulation capacity of 34.1%, and a phase change temperature of 43.8°C compared with that of pure $VO_2$ film.

The high phase transition temperature of $VO_2$ films is a major challenge for their application in smart windows. We describe that doping, especially multi-element doping, can effectively reduce the phase transition temperature and balance the optical properties. The phase transition temperature of $VO_2$ films can be lowered in other ways besides doping, such as by adding intrinsic defects and strains, but these methods give up the thermochromic properties. $VO_2$ nanoparticles, on the other hand, have been improved in how they are made and how their surfaces are treated. Nucleo-shellization and hybridization, for example, have been shown to be good ways to balance the phase transition temperature and thermochromic properties. $SiO_2$, $TiO_2$ and ZnO are all used as $VO_2$ coatings in the enclosure because they have high visibility or infrared transparency (Shen et al., 2021). Chen et al. described a way to directly coat vanadium dioxide nanoparticles with a layer of zinc oxide shell. The zinc oxide acts as a protective layer and an anti-reflective layer on the outer layer, and it has a higher visible light transmittance (51.0%) and sunlight energy modulation amplitude (19.1%), which means it is more stable (Chen et al., 2017).

As the preparation process of vanadium dioxide materials matures, researchers have developed an increasing number of preparation methods. When you mix vanadium dioxide film with other thermochromic materials (Y. Zhou et al., 2015) and make them more stable, you can make the film work better and use the materials in smart windows in a better way. In general, vanadium dioxide films have a wide range of applications in the field of smart windows, but the higher phase transition temperature, lower sunlight energy modulation and visible light transmittance of vanadium dioxide need to be further improved to meet the use standards. Considering the commercial use of smart windows, the large-area preparation process, production cost and service life are all factors that cannot be ignored in the research of vanadium dioxide film in the field of smart windows (Cao et al., 2020; Cui et al., 2018; Zhou et al., 2019).

## 5.2 Switches of photoelectric and terahertz

Switches are becoming more and more widely used in our lives because vanadium dioxide undergoes a metal-semiconductor phase transition before and after a phase change, resulting in a change in its resistance. Vanadium dioxide film's phase transformation characteristics make it suitable as a special material in photoelectric switches. Figure 9C is a temperature-resistance curve of vanadium dioxide films (Reese et al., 2004). The photoelectric switch uses the reversible phase change of the vanadium dioxide film, which is higher than the $VO_2$ phase change temperature, and the $VO_2$ film shows a metal state with low resistivity, at which time the current can pass through and the switch is turned on; when the phase change temperature is lower than the $VO_2$ phase change temperature and shows a semiconductor state, the resistivity suddenly increases and makes it difficult for the current to pass through, resulting in the switch being disconnected. Therefore, controlling the temperature change of the vanadium dioxide film realizes the automatic control of the switch. Compared to traditional switches, the ceramic photovoltaic switch prepared from vanadium dioxide film not only works under high current but also has a nanosecond counterresponse time, making it suitable for high-speed photovoltaic switches with a larger application area and longer service life.

$VO_2$ film can also function as terahertz switches, in addition to photoelectric switches. Schalch J. et al. designed a wideband electrically tuned $VO_2$ metamaterial terahertz switch with suppressed reflection. Figure 9D shows the switch structure, which consists of four layers. They are double-layer metamaterials with an anti-reflection structure, a silicon substrate, $VO_2$ and staggered gold electrodes. The double-layer metamaterial structure on top of the device forms high-resistance silicon, and the specific parameters of the whole device are: $D_1$ = 92 μm, $D_2$ = 74 μm, $H_1$ = 30 μm, $H_2$ = 45 μm. The thickness of the silicon substrate is $T_{Si}$ = 410 μm, the thickness of $VO_2$ is $T_{VO2}$ = 0.2 μm, and the thickness of the gold interleaved electrode is $T_{Au}$ = 0.15 μm. Before the phase change, the film transmits the majority of the terahertz, but after the transition, the terahertz wave experiences low reflection and transmission, resulting in the dissipation of most of the energy as heat (Schalch et al., 2020).

## 5.3 Temperature sensor

$VO_2$ is a metal oxide; its optical, electrical, magnetic, and thermal properties are variable, so it can be applied to different types of sensors, such as biosensors, pressure sensors, temperature sensors, etc. The function of the sensor is to convert the perceived information into electrical signals or other readable signals, which can be used to detect, process and display the information (Chang et al., 2015).

Kim et al. (2007) used $Al_2O_3$ substrate epitaxy to grow $VO_2$ films to prepare critical temperature sensors that can be used for programming. (Kim et al., 2007). The sensor structure can measure the change of conductivity by applying voltage to the vanadium dioxide film through the Ni electrode with ohmic contact at both ends. The detection temperature range of the sensor can be adjusted by applying external voltage regulation, and the bidirectional detection of tensile stress and compressive stress can be realized. In addition, Azharudeen A. M. et al. used an enhanced mesoporous $VO_2$/PVA nanocomposite electrochemical sensor to measure glucose (Mohamed Azharudeen et al., 2019). The measurement results show that the biosensor has high selectivity, high stability and high sensitivity. They compared the results of measuring glucose in blood samples with those of a clinical blood glucose analyzer. The relative error of the two samples was less than 4%.

## 5.4 Terahertz modulators

The terahertz wave in the excitation spectrum spans the microwave and infrared bands, and it covers a frequency of 0.1~10 Hz (Rahm et al., 2013). Terahertz waves possess significant technical value and can transmit crucial physical information, which finds applications in wireless communication, non-destructive testing, imaging, spectroscopy, etc. This information requires modulators, absorbers, and filters to manipulate terahertz waves. $VO_2$ film can modulate the terahertz wavefront, allowing for adjustable terahertz transmittance, absorption, and reflectance, under the external stimulus of phase change temperate. In its insulated state, $VO_2$ is almost completely clear to terahertz waves. However, when it changes to its metallic state, the transmittance to terahertz waves changes because the concentration of free carriers changes during the phase transition. This feature provides a large modulation depth and a low 1 L significance requirement for $VO_2$-based terahertz manipulation devices (Shi et al., 2011; Zhao et al., 2012; 2013).

Recently, the combination of $VO_2$ film and metamaterials has become a popular area of research. This is because the $VO_2$ film's performance in ultrafast phase transition works well with the THz wave resonance properties of metamaterials. Controlling the interaction between terahertz radiation and metamaterials allows for the modulation of the output response using metamaterials. Y. Zhao et al. proposed a THz phase shifter based on $VO_2$ combined capacitance-inductance resonance and dipole resonance, which generates a larger phase shift by dynamically modulating THz waves. The phase shifter structure consists of a ring-dumbbell composite resonator (RDCR) cell that is a mixture of a circular SRR and a vertical dumbbell dipole resonator (DR). The 11 × 10 × 0.284 micron $VO_2$ nanofilm was fabricated on a quartz substrate by photolithography and embedded in the gaps on both sides of the RDRCR (Zhao et al., 2018).

Electrical tuning is one of the most commonly used methods for terahertz modulation. Cai et al. (2018) developed a $VO_2$-based hybrid multifunctional metasurface (Figure 10A) to demonstrate electrically triggered switching and photonic memory effects in the teraherz region using an asymmetric split-ring resonator fabricated by substrate integration (Cai et al., 2018). Simulating the intracellular electric field distribution curves per unit of $VO_2$ insulating state and metallic state at 0.864 THz and 0.63 THz (Figure 10B) demonstrated the electric dipole resonance at two different resonance frequencies during the $VO_2$ phase transition. The goal of the experiments was to look into the terahertz transmission properties of $VO_2$ hybrid metasurfaces with different current characteristics. The results showed that the electrically induced MIT threshold current is 0.4A, and the $VO_2$ asymmetric split-ring resonator uses 225 μW of power per unit cell. $VO_2$-based hybrid components in the terahertz band have excellent switching performance (Figure 10C). The modulation depth is 54% at 0.63 THz and 36% at 0.864 THz, and the electrically triggered modulation speed is about 2 s. In conclusion, combined with the $VO_2$ phase change in thin film properties, it is helpful to achieve high-performance terahertz modulators.

## 5.5 Reconfigurable metasurfaces

Metasurfaces are two-dimensional metamaterials that can flexibly control the intensity, phase, polarization, frequency, angular momentum, and other characteristics of electromagnetic waves through artificially designed subwavelength electromagnetic structures arranged periodically or aperiodically on a plane. Compared to traditional bulk optical devices, optical metasurfaces have the characteristics of being lightweight, compact, and easy to integrate, and have good application potential in fields such as optoelectronic detection, imaging, and sensing. In recent years, research on optical reconfigurable metasurface devices has been carried out to meet the application needs of multi-dimensional detection, all optical modulation, adaptive beam deflection, and zoom lenses, and preliminary prototype verification has been achieved.

In reconfigurable metasurfaces, reconfigurable metasurfaces based on $VO_2$ phase change materials have advantages such as a large tuning range, fast tuning speed, low power consumption, and all-solid state. However, related devices still have problems such as low efficiency and a single control dimension, which restrict their practical applications. Therefore, the development of new $VO_2$-based thin film materials with low loss and a large tuning range and the design and preparation of high-transmittance, multi-dimensionally controllable metasurface structures are important directions for the development of this technology.

Based on $VO_2$ phase change materials, a series of reconfigurable surface plasmon metasurfaces and all dielectric metasurfaces have been used to achieve high efficiency and multi-dimensional control of devices. Future applications can be explored in the following areas: 1) High-value phase change materials have a significant impact on the performance of reconfigurable metasurfaces, but currently there is still a lack of development and optimisation for new optical materials. Therefore, in future work, the phase change optical properties of phase change material $VO_2$ should be further optimised through band modulation, and $VO_2$-based phase change materials with low optical losses before and after phase change should be developed. 2) Complete the point-by-point control design of a flexible reconfigurable metasurface based on $VO_2$ and achieve adaptive beam focusing in experiments; Design infrared camouflage devices with adjustable infrared radiation direction based on flexible device manufacturing methods.

## 5.6 Infrared imaging

The high temperature coefficient of resistance of $VO_2$ gives it excellent thermal sensitivity performance, which makes vanadium dioxide a high-quality, uncooled infrared focal plane detector array-sensitive material that is used to capture the real-time dynamics of infrared radiation from the detected object (Chen et al., 2007; De Almeida et al., 2004; Gurvitch et al., 2009). Vanadium dioxide has a strong phase transition stress from the monoclinic phase to the rutile phase. This means that there is a hysteresis effect when the phase changes from monoclinic to rutile. Therefore, in practical applications, some means are usually used to inhibit the phase transformation of vanadium dioxide and only retain the high temperature coefficient of resistance (Venkatasubramanian et al., 2009).

Doping is the main means to inhibit phase transition, and heavy doping can destroy the symmetry of vanadium dioxide grains, inhibit its growth, and eliminate the effects of phase transition. Gu et al. (2016) found that heavy doping of silver ions can inhibit the vanadium dioxide phase transition, while the conductivity of

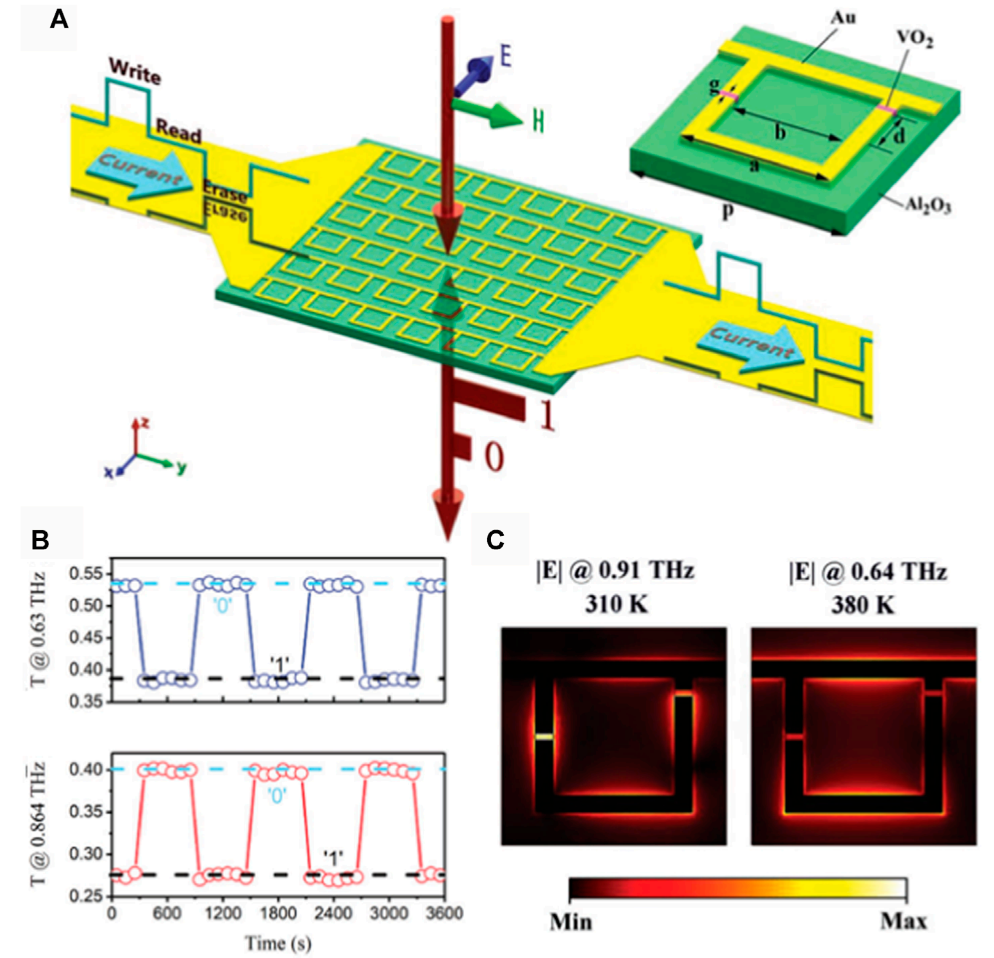


FIGURE 10
Terahertz modulator (Cai et al., 2018): **(A)** 3D schematic diagram of a $VO_2$-based hybrid metasurface with a terahertz wave incident in the *z*-direction and its electric field polarized in the *x*-direction, and an inset of a $VO_2$-based cell of a hybrid metasurface with geometric parameters; **(B)** The measured amplitude of transmission at 0.864 THz and 0.63 THz versus the time of bias current control; **(C)** Simulated electric field distribution curves in cell cells with insulated $VO_2$ at 0.91 THz and metal $VO_2$ at 0.64 THz.

vanadium dioxide films is improved and the thermal noise figure is reduced (Gu et al., 2016). A vanadium dioxide film with a room temperature resistivity of 0.24 Ω cm and a temperature coefficient of resistance greater than 5%k was obtained by heavy doping of silver.

Gu Deen et al. prepared $VO_2$ thin films without phase change at a deposition temperature of 200°C by doping with yttrium, a rare earth element. At the same time, the introduction of yttrium reduces the resistivity of the film by two orders of magnitude and retains the temperature coefficient of resistance of 1.5%K (Zhou et al., 2020). The elemental yttrium-doped $VO_2$ film has a unique structure of small crystalline particles spread out in the amorphous region. This makes the material less noisy and more stable.

$VO_2$'s high temperature coefficient of resistance makes it a potential heat-sensitive material, but its application hinders the inherent phase change hysteresis and phase change stress of $VO_2$. Doping inhibition of the $VO_2$ phase transition can obtain $VO_2$ films with a high temperature coefficient of resistance, high stability and low noise. The excellent thermal properties of this film will further improve the detection capability of uncooled focal plane detectors.

The high temperature coefficient of resistance of $VO_2$ films allows them to be used as detectors in the field of infrared imaging, especially for uncooled detectors based on $VO_2$ films. However, the disadvantages of uncooled detectors are lower sensitivity than cooled photon detectors, slow response speed, and high noise, which limit their performance applications. 1) Optimise the film preparation process: Adopt appropriate preparation methods, such as physical vapour deposition (PVD) or chemical vapour deposition (CVD), to obtain high-quality, dense $VO_2$ films and ensure the stability of their lattice structure and phase transition temperature. 2) Film surface treatment: The surface properties of $VO_2$ films are changed by chemical treatment, oxidation, ion implantation and other methods to enhance their absorption capacity and sensitivity to infrared radiation. 3) Optimise electrode design: design a suitable electrode structure to enhance the contact performance between the $VO_2$ film and the electrode and improve the signal response speed and stability. 4) Introduction of nanostructures: through nanostructure manipulation, such as nanoparticle doping, nanowire growth, etc., the interface area of $VO_2$ films can be increased, and the absorption efficiency and photoelectric conversion efficiency of infrared radiation can be improved. 5) Noise control: Reduce the impact of internal and external noise by improving the device structure and electronic design, such as using low-noise preamplifiers and optimising circuit layout. 6) Dynamic response range enhancement: The dynamic response range and sensitivity of $VO_2$ films can be improved by optimising the device structure and detection circuit design, such as by using multi-stage charge amplifiers and adding feedback circuits.

# 6 Summary and prospect

The development of a suitable $VO_2$ (M/R) films synthesis method is urgently needed for the commercial application exploration of research materials, and a large-scale, low-cost universal method is needed to obtain the $VO_2$ phase. The study of the synthesis of ideal $VO_2$ (M/R) films is an indispensable first step, and the synthesis of single-phase $VO_2$ (M/R) films with more uniform particle size, small particle size, better dispersion, perfect stoichiometry, and better crystallinity is a task to be completed. With the emergence of new light sources, $VO_2$ film research has gradually shifted from thermochromic to electrochromic and photochromic. For example, when $VO_2$ film is used in smart window coating, the research focus is on how to reasonably reduce the phase transition temperature and increase the visible light transmittance of the film. When $VO_2$ film is used as an uncooled infrared detector, the research focus is on the development of large-scale, wide-band, low-cost infrared focal plane arrays, reasonable control of its noise equivalent temperature difference, and improvement of the dynamic response range. In addition, the study of the electrical and thermal properties of $VO_2$ film and its combination with two-dimensional metasurface structures will be important research hotspots in the future.

As a thermochromic material, $VO_2$ film is not only used in the field of smart packaging but also in many fields such as photoelectric switches, smart windows, and the military. Using the principle that $VO_2$ film exhibits a semiconductor structure at low temperatures and a metal structure at high temperatures, the switches in the circuit can be directly controlled by adjusting the temperature to reach the phase change point, and the circuit can be automatically turned on and off (Chen et al., 2018; Markov et al., 2015). In addition, the abrupt change in transmittance of $VO_2$ film in the infrared band before and after phase change can be applied to control the relative on-off of the optical path (Wan et al., 2019). The concept of "smart window" has made $VO_2$ material a new type of energy-saving and environmentally friendly material (Cui et al., 2018). The heat of sunlight is mainly distributed in the infrared band, and $VO_2$ film has a high low-temperature transmittance and a low high-temperature transmittance in the infrared band, but its visible light transmittance hardly changes in the process (Ji et al., 2018d; Xu et al., 2018), Using this optical property, $VO_2$ powders can be prepared into flexible films, coatings, etc. for practical applications. The smart window can automatically adjust the solar intake according to the ambient temperature to achieve the effect of "warm in winter and cool in summer" while saving energy consumption. In addition, $VO_2$ film is considered to be an adaptive thermal camouflage material with a wide range of applications because it transmits and reflects infrared light waves before and after phase transition, which leads to changes in emissivity (Ji et al., 2018e; D; Liu et al., 2016). Adaptive thermal camouflage is a technique capable of creating a chameleon effect to adapt to the surrounding environment (Ji et al., 2018a), This technology can achieve a stealth effect in thermal imaging, and the lower the emissivity, the better the stealth effect. It is currently receiving more and more attention in many military applications.

Based on the description of $VO_2$ film synthesis methods and applications in the article, $VO_2$ film has become a breakthrough material with strong electron-electron correlation, but there are still some problems that need to be solved for the practical application of $VO_2$ film as a smart material. First of all, after the breakthrough of MIT in $VO_2$, the exact mechanism of MIT still needs a thorough explanation, and Mott or Perce assumptions alone are not enough to solve the origin of MIT, and linking the two theories may bring more understanding of MIT's origins. The stimulus response of $VO_2$ film to light fields, electrostatic fields, terahertz pulses, or stresses may complement the understanding of MIT mechanisms. Second, the exploration of the MIT mechanism is now limited to certain applications, such as smart windows and sensors. The popularity of thermochromic $VO_2$ film smart windows is increasing, but the practical difficulties of $VO_2$ coating need to be addressed, and the balance between Tc, transmittance, and solar modulation capacity can be extended through structural engineering, controlled porosity, and atomic-level doping. The lack of $VO_2$ material equipment limits the application of $VO_2$ and accelerates the research on $VO_2$ film application to meet the needs of the real world. Finally, the way to explore the practical application of $VO_2$ film is still a combination of simulation and experimental research. The coupling of $VO_2$ with other functional materials can effectively change the physicochemical properties, and the composites prepared from this material have potential advantageous properties.

Utilising the phase transformation characteristics of $VO_2$ films from semiconductors to metals requires a variety of ways to achieve this. In terms of temperature control, the phase change temperature of $VO_2$ is usually around 68°C. By controlling the ambient temperature, it is possible to control the phase transition from a semiconductor to a metal, thereby taking advantage of its characteristics. For example, temperature sensors and feedback control systems can be used to precisely control the temperature of $VO_2$ materials so that they achieve phase transitions within a specific temperature range. Achieved using light control, $VO_2$ materials are highly sensitive to light, especially in the near-infrared spectral range. By using lighting, the phase transition behaviour of $VO_2$ can be manipulated. For example, a phase transition from a semiconductor to a metal can be achieved by using an optical control switch or an optical modulator to control the phase transition state of a $VO_2$ material. In terms of electric field control, the electric field can also affect the phase transformation behaviour of $VO_2$ materials. By applying an appropriate electric field, the electronic structure of the $VO_2$ material can be changed, resulting in a phase change. For example, an applied electrode and a voltage source can be used to apply an electric field to control the phase transformation properties of $VO_2$ materials. In terms of strain control, strain can also have an impact on the phase transformation behaviour of $VO_2$

materials. By applying the appropriate strain, the lattice structure of the $VO_2$ material can be changed, resulting in a phase transition. For example, a mechanical device or piezoelectric material can be used to apply strain to control the phase transformation behaviour of a $VO_2$ material.

As a result, temperature control, optical control, electric field control, and strain control can all effectively use the semiconductor-to-metal phase transformation characteristics of $VO_2$. These methods can be selected and combined according to the needs of the specific application to achieve precise control of the phase transformation behaviour of $VO_2$ materials.

In short, compared with traditional functional crystals (KDP, RTAP, LN, and liquid crystal), $VO_2$ film has the characteristics of reversible changes in optical, thermal, and electrical properties, and its multi-parameter composite control and novel functional applications need to be further developed, and the goal of multi-functional integration of embedded systems needs to be realized. In view of its practical value in the field of military industry, the application of $VO_2$ film in infrared camouflage, multicolor electrochromic, and other fields will also be a research hotspot in the future.

## Author contributions

CW: Conceptualization, Investigation, Methodology, Writing–original draft. LF: Conceptualization, Investigation, Methodology, Writing–original draft. ZL: Conceptualization, Investigation, Methodology, Writing–original draft. JB: Methodology, Writing–original draft. SW: Supervision, Validation, Writing–original draft. XG: Supervision, Validation, Writing–original draft. JW: Supervision, Validation, Writing–review and editing. WY: Supervision, Validation, Writing–review and editing.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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