

## An Interesting Functional Phase Change Material VO<sub>2</sub>: Response to Multivariate Control and Extensive Applications in Optics and Electronics

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Under physical conditions such as  $T_C = 68$  °C, Vanadium dioxide (VO<sub>2</sub>) undergoes a reversible transformation from a monoclinic phase to a tetragonal rutile phase. This transformation is accompanied by a series of changes in physical properties, including transmittance, conductivity, and refractive index, which make it an excellent functional material. Based on this, VO<sub>2</sub> has been extensively researched and applied in the fields of electronics and optics, yielding remarkable results and making it a hot research material. This paper reviews the phase transition mechanisms and optical/electrical properties of VO<sub>2</sub>, as well as its phase transition hysteresis. From the application perspective, this paper summarizes the modulation content under various external excitations and the element doping effects. Finally, this paper summarizes the classic VO<sub>2</sub>-based devices, and points out the development direction and potential of VO<sub>2</sub> in optics and electronics. This review provides a systematic summary of VO<sub>2</sub>, which is useful for its practical applications.

## 1. Introduction

In 1959, F. J. Morin<sup>[1]</sup> first reported the dramatic change in the conductivity of VO<sub>2</sub> caused by temperature change, which proved the insulator-metal transition (MIT) behavior of VO<sub>2</sub>, and now VO<sub>2</sub> has become a research hotspot in the field of condensed matter physics and phase change materials. VO<sub>2</sub> has been shown to

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undergo reversible MIT at 68 °C, accompanied by structural transition from monoclinic (P2<sub>1/c</sub>) to tetragonal rutile  $(P4_{2/mnm})^{[2]}$  In the process of VO<sub>2</sub> insulator-metal transition, the band structure changes dramatically, the band gap changes from  ${\approx}0.67$  to 0 eV, the Fermi energy level passes through from  $d_{II}$  and antibonding  $\pi^*$  band, and physical properties such as conductivity and light transmittance change abruptly, in which resistance/conductivity can achieve a large jump of more than three orders of magnitude, and infrared light transmittance produces huge modulation.<sup>[3]</sup>

As a strongly correlated material, in addition to classical thermal modulation,<sup>[4]</sup> external excitations such as electric field,<sup>[5]</sup> magnetic field,<sup>[6]</sup> strong light,<sup>[7]</sup>

and strain<sup>[8]</sup> can also modulate VO<sub>2</sub> insulator-metal phase transition, and the effect is obvious. Among them, external electric field excitation, as an efficient and convenient modulation method, is widely used in VO2-based devices, and the mechanisms of effect is divided into joule heating,<sup>[5a,9]</sup> pure electric field mechanism<sup>[10]</sup> and electrochemical mechanism.<sup>[11]</sup> In addition, external electric field excitation derives many efficient device modulation structures, such as sandwich structure, planar structure, field effect transistor FET structure and ionic liquid gating structure, in recent years, the modulation method of ionic liquid gating has developed rapidly, through the electric field to control ion migration, which indirectly triggers phase transition in a non-thermal way by controlling ion migration through electric field, which is attractive in new generation electronic devices.<sup>[5c,12]</sup> At present, the phase transition mechanism of VO<sub>2</sub> is still controversial, one explanation is the Mott-Hubbard mechanism: VO<sub>2</sub> is regarded as a strongly correlated electronic system, and its phase transition is caused by strong interaction between electrons;<sup>[13]</sup> Another explanation is the Peierls mechanism: changes in crystal structure eventually lead to changes in the band structure, causing phase transition in the material.<sup>[14]</sup> It has also been suggested that the VO<sub>2</sub> phase transition comes from the combined effect of the above two mechanisms.<sup>[15]</sup> Even if the phase transition mechanism of VO<sub>2</sub> is unknown, its special phase transition properties and multiple modulation methods are widely used in the design and production of optical/electrical devices, and satisfactory results have been achieved in the fields www.advancedsciencenews.com

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**Figure 1.** a) The lattice structure of tetragonal rutile VO<sub>2</sub> (left) and monoclinic VO<sub>2</sub> (right). Reproduced with permission.<sup>[2b]</sup> Copyright 2014, Springer Nature. Schematic of the VO<sub>2</sub> band structure in the metallic b) and insulating c) states.

of optical and electrical switches, modulators, sensors, and smart windows.  $^{\rm [16]}$ 

In this paper, we have reviewed the phase transition mechanism of  $VO_2$  and the changes of electronic and lattice structures in the process of phase transition, gives an overview of the changes in optical and electrical properties and hysteresis caused by the phase transition, summarizes the modulation methods of  $VO_2$  phase transition from the perspective of external excitation of devices, discusses the influence of elemental doping, and finally summarizes the application progress of  $VO_2$  material in the field of optoelectronic devices in recent years, looks forward to the development prospect of  $VO_2$ , and provides help for the application process of vanadium dioxide.

# 2. VO<sub>2</sub> Phase Transition Structure Change and Mechanism

## 2.1. Crystal Structure and Electronic Structure Changes

The crystal structural phase transition (SPT) accompanying the metal-insulator phase transition (MIT) has always been the research focus of VO<sub>2</sub> materials, which is closely related to temperature change. As shown in the **Figure 1a**, at high temperature (>  $\approx$ 340K), VO<sub>2</sub> is in a tetragonal rutile structure (R, P4<sub>2</sub>/mnm) and the V atoms are surrounded by O octahedra; when at low temperature (<  $\approx$ 340K), V<sup>4+</sup> ions dimerize along the c<sub>R</sub> direction, and the V-V chain length changes from the original 2.85 Å to the alternating distribution of 2.60 and 3.19 Å, and the V-V dimer is

slightly deflected relative to the  $c_R$  axis, forming VO<sub>2</sub> monoclinic phase (M, P2<sub>1</sub>/c) crystals with reduced symmetry of crystals.<sup>[2b]</sup> In addition, during the transition of VO<sub>2</sub> from M1 phase to R phase, there are also intermediate structures near the phase transition temperature, such as M2 phase, M3 phase and T phase.<sup>[17]</sup> The existence of intermediate structures indicate that the structure phase transition of VO<sub>2</sub> is a gradual process, which provides an idea for studying VO<sub>2</sub> hysteresis curves. In some temperaturedependent Raman spectroscopy or XRD spectroscopy studies, it was found that physical properties and structural changes of VO<sub>2</sub> did not occur simultaneously, and that the SPT changed before MIT. However, in some VO<sub>2</sub> application designs, the SPT and MIT are not over-partitioned, and it is basically determined that the optical and electrical properties change at the same time as the structure changes.

The structural phase transition in VO<sub>2</sub> is accompanied by a change in the structure of the electron band near the Fermi level (EF): according to the model proposed by John B. Goodenough, at high temperature, the 3d electron orbital of V ions is split by the crystal field into a combination of low-energy  $t_{2g}$  states and high-energy  $e^{\sigma}_{g}$  states. Small orthogonal components of the crystal field associated with different equatorial and apical V-O bond distances further split the  $t_{2g}$  orbital into two  $d_{\pi}$  orbitals ( $\pi$  and  $\pi^*$ ) and one  $d_{//}$  orbital. The  $e^{\sigma}_{g}$  orbital split into the  $\sigma$  orbital and the anti-bond  $\sigma^*$  orbital. The  $e^{\pi}_{g}$  orbital and  $e^{\sigma}_{g}$  orbital are hybridized with the O  $_{2p}$  orbital to form a low-energy bonding combination dominated by O  $_{2p}$  features and a high-energy antibonding combination dominated by V  $_{3d}$  features (Figure 1b). For VO<sub>2</sub>(R), the

d<sub>//</sub> band and the antibonding π<sup>∗</sup> band overlap each other and are partially filled, through which the Fermi level passes and VO<sub>2</sub> takes on metallic properties. When VO<sub>2</sub> changes from a metallic state to an insulating state (monoclinic phase), the dimerization of V atoms intensifies, as shown in the Figure 1c, resulting in the d<sub>//</sub> band splitting into two parts: the d<sub>//</sub>\* band with higher energy, and the d<sub>//</sub> band with lower energy full of electrons, while the π<sup>∗</sup> moves upwards above the Fermi level, forming a band gap of ≈0.7 eV, so that VO<sub>2</sub> exhibits insulating properties.<sup>[3f,18]</sup>

Studying the crystal structure and electronic structure changes during VO<sub>2</sub> phase transition is crucial to explore the VO<sub>2</sub> phase transition mechanism and study the related dynamic processes. Only through a thorough understanding of the underlying mechanisms of the phase transition in the VO<sub>2</sub> system, can we effectively control the phase transition process of VO<sub>2</sub>, achieve optimal material properties, and expedite the application of VO<sub>2</sub>.

#### 2.2. Phase Transition Mechanism

At present, the proposed VO<sub>2</sub> phase transition mechanisms mainly include: (i) Peierls mechanism based on crystal structure change; (ii) Mott-Hubbard mechanism based on carrier concentration change; (iii) The two mechanisms work together. The controversy over the mechanism stems from whether the VO<sub>2</sub> phase transition is electron-lattice interaction or electron-electron interaction. The role of V-V pairing structural effects versus electron correlations for the splitting of the  $a_{1g}$  orbitals remains open to debate. In order to understand the mechanism of the VO<sub>2</sub> phase transition, scientists have done a lot of researches and made great progress.

First, the Peierls mechanism believes that VO<sub>2</sub> lattice distortion leads to changes in atomic periodic potential energy, changes in potential fields lead to changes in band structure, and then band gap changes, and finally VO2 undergoes metal-insulator phase transition. This is a phase transition interpretation based on electron-phonon strong interaction. Ishiwata et al.[19] found that lattice distortion is consistent with changes in the electron states around E<sub>F</sub>, which confirms the role of the Peierls mechanism in energy splitting in the  $a_{1g}$  state. In addition, Budai et al.<sup>[2b]</sup> reported from the perspective of the entropy contribution of VO<sub>2</sub> phase transition that the entropy driving MIT in VO<sub>2</sub> is dominated by strongly anharmonic phonons rather than electronic contributions, and provided a direct determination of phonon dispersions, affirming the key role of the Peierls mechanism in VO<sub>2</sub> phase transition. However, some works claim that VO<sub>2</sub> SPT and MIT are not simultaneous, realizing the decoupling of MIT and SPT, thus denying that the structure drives phase transition.<sup>[10a,20]</sup> In addition, the Peierls mechanism does not answer well the case of 0.6 eV band gap in VO<sub>2</sub> (M1) and the presence of intermediate phases (M2, M3, T) of VO2 during phase transition.<sup>[21]</sup>

Later, it was found that Coulomb repulsion indeed plays a major role in opening the bandgap, which means that electronelectron interaction may be the driving source of the VO<sub>2</sub> phase transition.<sup>[22]</sup> Unlike the Peierls mechanism, the Mott-Hubbard mechanism explains the mechanism of VO<sub>2</sub> phase transition ELECTRONIC MATERIALS

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based on electron-electron interaction: when the free carrier reaches a certain concentration, the occurrence of VO<sub>2</sub> phase transition can be directly triggered. In some works, the existence of the monoclinic and correlated metal (MCM) phase has opposed the causal relationship between SPT and MIT, strongly demonstrating the key role of the Mott mechanism in the VO<sub>2</sub> phase transition.<sup>[23]</sup> In addition, under the action of electric field, the phase transition of VO<sub>2</sub> can be directly triggered by carrier injection, which also rejects the theory of structure-induced phase transition.<sup>[24]</sup> However, the Mott mechanism cannot well explain the second half of the phase transition process and the VO<sub>2</sub> phase transition dominated by electron-phonon action in some situations.

Thus, some researchers begun to point the mechanism of the VO<sub>2</sub> phase transition to the Peierls mechanism working together with the Mott-Hubbard mechanism, also known as the Peierlsassisted phase transition. Liu et al.<sup>[25]</sup> quantified microbeam infrared spectra under conditions of temperature and stress alteration and found that a first-order structural transition strongly affected by the carrier-carrier interaction meaning that carriercarrier interaction increase the effect of Peierls pairing in VO<sub>2</sub> and together lead to phase transition. Chen et al.<sup>[15a]</sup> attributed the bandgap opening of about 0.2 eV in the initial stage of MIT to the electron-correlated driven Mott transition, and attributed the bandgap increase from 0.2 to 0.8 eV caused by the rapid increase of the twisting angle of the V-V chain to the structure-driven Peierls transition, revealing that there are electron-correlated driven Mott transition and structure-driven Peierls transition in the MIT process of VO<sub>2</sub>. Likewise, Kim et al.<sup>[26]</sup> revealed the Mott IMT in the nondistorted monoclinic nanodomain between 55 and 63 °C and the distortion-assisted SPT above 60 °C by studying the diffraction anomalous near-edge structure (DANES) to measure X-ray absorption spectra.

In short, the current VO<sub>2</sub> phase transition mechanism is still controversial, whether it is structure-driven phase transition or carrier-driven phase transition, it has been experimentally verified, which also indicates that the two are more likely to work together. Moreover, a large number of studies have shown that the VO<sub>2</sub> phase transition mechanism may be closely related to the triggering mechanisms. However, the determination of the VO<sub>2</sub> phase transition mechanism needs more experiments to verify.

## 3. Changes in Optical and Electrical Properties Caused by VO<sub>2</sub> Phase Transition

When VO<sub>2</sub> undergoes insulator-metal phase transition, it is accompanied by changes in many physical properties, the first of which is observed is the change of electrical property. With the deepening of research and the improvement of experimental instruments, scientists have found that the phase transition of VO<sub>2</sub> is accompanied by changes in optical properties and other interesting physical properties, which makes VO<sub>2</sub> gradually become the object of attention in the field of device preparation. Studying the property changes brought by VO<sub>2</sub> phase transition is not only helpful to explore its phase transition mechanism, but also provides physical property modulation data of VO<sub>2</sub> material, which is of great significance for

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Figure 2. The change of resistance measured with the amount (1, 3, 5, and 10 V) and the number (up to 10 times) of voltage pulses of a single  $VO_2$ nanowire. Reproduced with permission.<sup>[9]</sup> Copyright 2013, WILEY-VCH.

the practical application of VO<sub>2</sub>. This chapter mainly discusses the research progress of optical and electrical properties changes caused by VO<sub>2</sub> phase transition, and describes the thermal hysteresis phenomenon, which is innovative in VO2-related review reports.

## 3.1. Changes in The Optical and Electrical Properties

In VO<sub>2</sub> system, the coupling of lattice, charge, spin and orbit changes the optical, electrical and other physical properties of VO<sub>2</sub> near the phase transition point.<sup>[21]</sup> The first physical properties studied were electrical properties, and Morin<sup>[1]</sup> first discovered that VO<sub>2</sub> had a sudden change in conductivity near the phase transition point, confirming the phase transition behavior of VO<sub>2</sub>. Since then, numerous works have shown that the VO<sub>2</sub> phase transition is accompanied by significant changes in electrical properties. Among them, resistivity/conductivity is used as a key parameter to evaluate the change of conductivity, and the resistance/conductivity change of nanostructures can be achieved by preparation technology of more than 3 orders of magnitude, or even 5 orders of magnitude.

Surface topography is a key factor affecting the conductivity of thin films, the smoother the surface morphology, the better the conductivity.<sup>[27]</sup> In addition to controlling the morphology of the film through deposition parameters, the substrate also has a great influence on the topography. For instance, Cheng et al.<sup>[28]</sup> chose hexagonal 6H-SiC, which is similar to the VO<sub>2</sub> lattice structure, as a substrate to deposit VO<sub>2</sub> films, and achieved a wide range of resistance transition of  $5.66 \times 10^4$  by controlling the deposition parameters. The large conductivity change caused by the phase transition of VO<sub>2</sub> makes it a high-quality material for electronic devices such as switches and transistors.

There is phase coexistence during the VO<sub>2</sub> insulator-metal phase transition, and the M/R phase ratio is different in different phase mixing states, and the proportion can be controlled by externally applied energy (thermal, electric, light, etc.), resulting in multiple resistance.<sup>[9,29]</sup> In 2013, Bae et al.<sup>[9]</sup> applied voltage pulses of different value and number to VO<sub>2</sub> nanowires, as shown in the Figure 2, using self-Joule heating, to achieve multistage jumps in a large range of nanowire resistance, and even in a small range can control changes in resistance less than one order of magnitude. Based on the multiple resistance characteristics, VO<sub>2</sub> has application potential in the field of memory devices.

In addition, the examine of changes in the optical properties of VO<sub>2</sub> has been around for a long time. After Morin used changes in conductivity to prove the phase transition of  $VO_2$ , and in 1966, Barker of Bell Labs.<sup>[30]</sup> found that when T>T<sub>c</sub>, almost all VO<sub>2</sub> polarization spectrum showed high reflectivity similar to typical metallic or free carrier behavior, and the fitted infrared reflection spectrum showed significant changes compared to the low temperature phase. In the decades that followed, the question of changes in optical properties due to the phase transition of VO<sub>2</sub> was gradually answered.

When  $VO_2$  is in the insulating phase, the intrinsic band gap is  $\approx 0.67 \text{ eV}^{[31]}$  and the optical band gap is  $\approx 2.5 \text{ eV}^{[32]}$  and according to equation (6):  $(\alpha h v)^2 = A(h v - Eg)$ , it can be seen that the wide optical bandgap leads to a low absorption coefficient of the infrared light,<sup>[31–33]</sup> and the existence of the intrinsic bandgap puts VO<sub>2</sub> in the insulating phase with few free carriers, which further reduces the light absorption, so that  $VO_2(M)$  has a high IR transmittance







**Figure 3.** a) Experimentally measured resistance of the VO<sub>2</sub> sensor as a function of temperature during the fully reversible heating and cooling cycle using substrate heating; b) Temperature-dependent TCR value of VO<sub>2</sub> in the major heating and cooling curves across the phase-change region. Reproduced with permission.<sup>[49]</sup> Copyright 2023, Royal Society of Chemistry. c) Refractive indices (n and k) of VO<sub>2</sub> film with 160 nm thickness deposited on glass, measured by ellipsometry. Reproduced with permission.<sup>[39]</sup> Copyright 2023, Elsevier B.V. d) DSC spectrum of the bimodal VO<sub>2</sub>(M);<sup>[3d]</sup> e) Temperature evolution of k during the heating and cooling processes of VO<sub>2</sub>. Reproduced with permission.<sup>[50]</sup> Copyright 2018, American Physical Society.

compared to VO<sub>2</sub>(R).<sup>[34]</sup> During the insulator-metal transition, the Fermi level is in the  $d_{11}$  band, VO<sub>2</sub> appears as a metallic state, the intrinsic band gap disappears, with the intrinsic bandgap disappearing and the optical bandgap almost unchanged, but with the increase of the concentration of free carriers in the energy bands and the absorption of electrons by intra-band leptons in the V<sub>3d</sub> energy band, the reflectivity and infrared absorption increase, so the infrared transmittance decreases.<sup>[34b,35]</sup> In addition, the band gap can be doped widened<sup>[34a]</sup> or narrowed<sup>[18a]</sup> to improve the transmittance of VO<sub>2</sub> films in the visible range or to increase their near-infrared absorption. It has also been suggested that there is a mathematical relationship between the widening of the band gap and the doping content.<sup>[36]</sup> Details and mechanisms of doping are discussed in Section 5. Finally, the microstructure of the film also has a significant impact on the optical properties of VO<sub>2</sub>.<sup>[37]</sup> For instance, surface roughness affects the reflectivity of the film structure,<sup>[36]</sup> and film porosity also affects light transmittance.[38]

It is of great significance to study the changes of optical and electrical properties caused by  $VO_2$  phase transition, which is the premise of  $VO_2$  application in the field of electronics and optics. At present, the excellent physical modulation performance of  $VO_2$  nanostructure can be realized, and it has broad application prospects in the future, but the theoretical exploration and

performance optimization of  $\rm VO_2$  optical and electrical properties still need to continue.

## 3.2. Study of Thermal Hysteresis

The metal-insulator phase transition of VO<sub>2</sub> belongs to the firstorder phase transition, and there is latent heat in the phase change, so superheating and supercooling are required during the heating and cooling process to trigger the phase transition, resulting in thermal hysteresis. Thermal hysteresis is one of the distinctive features of phase change materials. The thermal hysteresis width is an important criterion to measure the degree of hysteresis, and it is also a key parameter to consider in the application of VO<sub>2</sub> materials. In the case of VO<sub>2</sub>, thermal hysteresis loop width ( $\Delta$ H) is calculated from the refractive index, transmittance, electrical resistivity, temperature coefficient of resistance (TCR), thermal conductivity and differential scanning calorimetry (DSC) (**Figure 3**), and the expression is<sup>[39]</sup>:

$$\Delta H = T_{c,heating} - T_{c,cooling} \tag{1}$$

where  $T_{c,heating}$  and  $T_{c,cooling}$  correspond to the phase transition temperature of VO<sub>2</sub> during heating and cooling process, respectively. The physical mechanisms affecting  $\Delta H$  are complex, first,

according to the nucleation theory, the strain energy determines the hysteresis width by the change in shear energy during heating and cooling,<sup>[40]</sup>

$$\Delta H = \frac{\frac{1}{2}\eta G\gamma^2}{\Delta S} \tag{2}$$

where  $\eta$  is the shape parameter, G is the shear modulus,  $\gamma$  is the shear strain, and  $\Delta S$  is the entropy changes. As can be seen from Equation (2), the morphology and roughness of the VO<sub>2</sub> nanocrystals determine the  $\eta$  value, which affects the hysteresis width. Experiments show that for the flake nanocrystalline VO<sub>2</sub> prepared by magnetron sputtering, the  $\eta$  tends to be close to 0, the hysteresis width is also close to 0, and the hysteresis curves basically coincide.<sup>[40a,41]</sup> In addition, the VO<sub>2</sub> film prepared by flexible substrate has a small shear modulus G due to its flexibility, and can also maintain a low hysteresis width.<sup>[40b]</sup>

Second, when the effect of stress on hysteresis is negligible (the film thickness is greater than the critical thickness), the effect of the interfacial energy can be analyzed,<sup>[42]</sup>

$$\Delta T_r = \frac{2\gamma}{r_c \Delta S} \tag{3}$$

where  $\Delta T_r$  is the deviation from the equilibrium transition temperature,  $\gamma$  is the interface energy,  $r_c$  is the critical size of the stable nucleus, and  $\Delta S$  is the change in entropy between the two phases. There was a positive correlation between  $\Delta H$  and  $\Delta T_r$ .<sup>[42a,c]</sup> The interfacial energy is related to the grain boundary orientation, and studies have shown that large-angle, randomly oriented boundaries will lead to greater hysteresis,<sup>[43]</sup> and the choice of substrate will also significantly affect the hysteresis width.<sup>[44]</sup> The effect of grain size on hysteresis width can also be deduced from Equation (3): the grain size is proportional to  $r_c$ , so the hysteresis line width is inversely proportional to the average grain size of VO<sub>2</sub> films.<sup>[42a,44a]</sup> The size of the grain size can be controlled by controlling the partial pressure of oxygen during the deposition process.<sup>[44b]</sup>

In addition, defects are also thought to be the origin of hysteresis, and as the density of nucleating defect increases, the driving force required to produce the activated nucleation sites decreases, so high defect density often leads to narrow hysteresis width.<sup>[43,45]</sup> Doping is considered to be an effective way to control the nucleation density of defects, and it is easy to achieve narrow or even no hysteresis.<sup>[46]</sup> In addition, the relationship between the aggregation and hysteresis of VO<sub>2</sub> particles has also been studied, and experiments have shown that the aggregation of VO<sub>2</sub> can reduce or even eliminate the inverse relationship between grain size and hysteresis, and the degree of agglomeration is affected by the annealing time.<sup>[44a]</sup> In addition, the thermal hysteresis width is different for different physical properties (light transmittance, resistance, etc.). At present, there is no unified physical explanation for hysteresis, but we believe that the hysteresis of VO<sub>2</sub> in experiments is often affected by many of the above factors. Therefore, when designing VO<sub>2</sub>-based devices, the  $\Delta H$  can be adjusted by methods of doping or adjusting the preparation parameters to obtain the ideal thermal hysteresis width.

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During the electrically excited VO<sub>2</sub> thermal phase transition, the Joule thermal effect causes the thermal hysteresis loop width of the film to widen, resulting in a longer recovery time of the phase transition, which adversely affects the response speed of the device.<sup>[38]</sup> Therefore, obtaining narrow hysteresis loops of the VO<sub>2</sub> film is significant for improving the performance of VO<sub>2</sub>-based devices. Among them, doping has obvious effect on shortening  $\Delta$ H. For example, Huang et al.<sup>[47]</sup> doped 1 at.% Hf in VO<sub>2</sub> films to achieve a narrow thermal hysteresis width of  $\Delta$ H = 1.9 K. Even, Yang et al.<sup>[48]</sup> used Ni doping to eliminate the magnetic moment-temperature hysteresis based on the principle of magnetoelastic coupling between Ni and VO<sub>2</sub> films through reversible structural phase transition.

In addition, optimizing the preparation conditions can also achieve high sharpness thermal hysteresis. For example, Makarevich et al.<sup>[51]</sup> optimized the annealing process of VO<sub>2</sub> films, and achieved the balance between dense fusion and structural continuity of the film under the annealing condition of 600 °C for 60 minutes, and successfully prepared VO<sub>2</sub> films with high hysteretic sharpness, in which  $\Delta$ H was only 0.7 °C. Zeng et al.<sup>[45]</sup> controlled the deposition thickness of the precursor film (V<sub>2</sub>O<sub>5</sub>) by film thickness monitor, grew VO<sub>2</sub> particles of different sizes, and finally achieved a minimum MIT temperature of 41 °C without hysteresis. Chang et al.<sup>[40b]</sup> proposed a new strategy for direct deposition of VO<sub>2</sub> thermochromic films on flexible substrates using Cr<sub>2</sub>O<sub>3</sub> structural template layer, which have hysteresis line widths of less than 1 °C.

The purpose of reducing the thermal hysteresis width is to reduce the effect of hysteresis and improve the response speed of the device, which is important in high-speed devices such as sensors and switches. In addition, the essence of  $\Delta$ H reduction is the reduction of the energy barrier, so the narrow thermal hysteresis curve width can improve the response of the device to ambient temperature, which can improve the energy-saving effect in smart windows and other similar devices.<sup>[52]</sup> However, in some application environments, especially memory devices such as memristors, the existence of VO<sub>2</sub> hysteresis characteristics is the key to device design, and the following briefly introduces memory devices designed with VO<sub>2</sub> hysteresis characteristics.

Bae et al.<sup>[9]</sup> first reported a two-terminal memristor memory based on a single VO<sub>2</sub> nanowire, which used the special hysteresis characteristics of the VO<sub>2</sub> I-V curve to maintain thermal stability in the hysteresis region through Joule heating generated by a specific bias voltage, and then used electrical pulses to achieve resistance switching.

In 2022, Jung et al.<sup>[53]</sup> designed an integrated hybrid  $VO_2$ -Silicon optical memory, as shown in the **Figure 4a**.  $VO_2$  is first kept within the IMT hysteresis at a constant voltage bias, and then excess carrier generation is induced by optical pulses, triggering the Mott-assisted Peierls structural phase transition (SPT) (Figure 4b). Since the phase of  $VO_2$  affected the electrical current of the device at the bias terminals and optical transmission of the underlying waveguide, the memory can be read out by the current or waveguide output transmission changes (Figure 4c,d).

Finally, the hysteresis loop represents the phase coexistence region, which provides an idea for explaining the  $VO_2$  phase transition mechanism. Based on the application of  $VO_2$ -based devices,





**Figure 4.** Waveguide-integrated  $VO_2$ -Si optical memory and its operating characteristics. a) Schematic of the waveguide-integrated  $VO_2$ -Si optical memory. SOD: spin-on dielectric, SMU: source measure unit. b) I–V measurement at a temperature of  $\approx$ 303 K (Red dotted line: voltage ramp up, blue dotted line: voltage ramp down), showing the IMT hysteresis. Yellow remark stands for the optical memory writing. The inset shows the top view of the measured device. Time trace of b) DC current and c) normalized optical transmission readout after turning off the laser pulse. Reproduced with permission.<sup>[53]</sup> Copyright 2022, American Chemical Society.

the influence of thermal hysteresis phenomenon on the design of VO<sub>2</sub>-based devices needs to be considered in many dimensions. In the future, the pursuit of zero hysteresis and efficient memory performance will be the two directions of VO<sub>2</sub> material in the application of hysteresis characteristics, and how to control hysteresis in a wide range will be an important topic in VO<sub>2</sub> applications.

# 4. VO<sub>2</sub> Phase Transition Modulation Methods In Optical and Electrical Devices

As a traditional phase change material, VO<sub>2</sub> can respond to various external excitations. Since the discovery of VO<sub>2</sub> insulatormetal phase transition at  $\approx$ about 340 K, VO<sub>2</sub> has been developed a variety of carrier-based or lattice-based insulator-metal phase transition modultion methods: external heating, external electric field, light, strain and magnetic field. In addition, the threshold of VO<sub>2</sub> phase transition adjustment field can be reduced by element doping, device-related film layer size adjustment and strain adjustment, so as to assist in adjusting VO<sub>2</sub> insulator-metal phase transition. This section mainly introduces the modulation method of VO<sub>2</sub> material phase transition based on the application aspect, and studies the development status of its control mode, so as to provide help for the diverse control of VO<sub>2</sub> insulator-metal phase transition in the future.

## 4.1. External Heating Source Modulation

The modulation of  $VO_2$  phase transition by external heating source is the most classic and direct device control method, but because it cannot change  $T_C$ , this modulation method is rarely discussed. However, we believe that this control method is currently the most extensive control method for  $VO_2$ -based devices, and there are still some key issues that need to be discussed.

The control method of VO<sub>2</sub> phase transition by external heating source appeared in a multitude of test experiments of VO<sub>2</sub> phase transition characteristics in the early stage. For example, Morin<sup>[1]</sup> directly heated by this method, and then observed a sudden change in VO<sub>2</sub> conductivity, proving the VO<sub>2</sub> insulationmetal phase transition behavior. Until now, all studies involving the phase transition of VO<sub>2</sub>, especially to test the degree of influence of other modulation methods on T<sub>C</sub>, mostly have been subjected to heat tests on samples to evaluate the thermochromic properties.<sup>[48]</sup>

In addition to being an ordinary auxiliary test, the external heating source control method plays an important role in the control of many VO<sub>2</sub> applications, and many heating control structures are derived from it. Kim et al.<sup>[55]</sup> designed a solid state passive switchable radiator for spacecraft thermal control, which installed a heating stage at the bottom of the device to simulate the







**Figure 5.** a) A sketch of a radiative thermal transistor. Reproduced with permission.<sup>[4b]</sup> Copyright 2019, American Physical Society. b) Schematic illustration of the experiment, where a pattern of orthogonal double-clamped microbridges was fabricated from VO<sub>2</sub> thin films grown on top of different MgO substrates and characterized by optical profilometry and electrical transport as a function of temperature. Reproduced with permission.<sup>[54]</sup> Copyright 2020, American Chemical Society.

temperature of the spacecraft to control the VO<sub>2</sub> phase transition, so as to control the emissivity of the device, realize a wide range of control of radiation power, and optimize the heat dissipation effect. Latella et al.<sup>[4b]</sup> designed a radiative thermal transistor, as shown in the **Figure 5a**, given a heating source, the state of the VO<sub>2</sub> gate is controlled by Peltier heating, thereby controlling the energy from the source radiation to the drain SiO<sub>2</sub>, achieving dynamic modulation and even amplification of the super-Planckian heat fluxes. Similarly, Manca et al.<sup>[54]</sup> built VO<sub>2</sub> microbridges on different substrates on Peltier, revealing the influence of different crystal structures on the strain dynamics and absolute strain values of the thin films, as shown in the Figure 5b.

Because external heating control has no effect on the phase transition characteristics of VO<sub>2</sub>, many related works are mainly based on the application level. In addition, the  $T_C$  value of the material can be reduced by other modulation methods, which makes it unnecessary to actively add a heating source for heating. In addition, when designing micro devices, the external heating source setting needs to consider the uniform heating of the device and the application environment space. Finally, the energy consumption of thermal control is higher than that of other control methods, and the tuning speed is much less than that of electrical tuning, and its control accuracy is low, and its application in the field of fast devices is limited. The following mainly summarizes the modulation method of VO<sub>2</sub>-based optical and electrical devices from the aspects of electrical, optical and strain control.

## 4.2. External Electric Field Modulation

In the last century, the problems of filamentary conduction and "S" type I-V curves in VO2-based devices have been studied, but it has not been explicitly stated that the external electric field can directly trigger VO<sub>2</sub> MIT.<sup>[56]</sup> In 2000, Stefanovich et al.<sup>[13b]</sup> used the metal/oxide/metal (MOM) structure, the carrier is injected to test switching delay time t<sub>d</sub>, which negated the original electrothermal model of VO<sub>2</sub> phase transition, and it is the first report that VO<sub>2</sub> phase transition can be triggered by electric fields or electron injection. Over the next two decades, the researchers used different device structures to achieve VO<sub>2</sub> phase transition controlled by external electric fields. It is found that the use of external electric field to control VO<sub>2</sub> can achieve rapid phase transition, improve the fatigue resistance of devices and reduce energy consumption, and the electric field control VO<sub>2</sub> phase transition (E-MIT) has gradually become a research hotspot in device preparation, and has achieved ideal application results.

#### 4.2.1. Modulation Structures

With the development of science and technology, the preparation level of  $VO_2$  nanostructures and related electronic devices has gradually improved, and researchers have begun to study different  $VO_2$ -based regulatory structures to study the mechanism, control and property changes of  $VO_2$  E-MIT, and on this



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**Figure 6.** a) Current-density J versus voltage V curve for VO<sub>2</sub>-based two-terminal Device. Reproduced with permission.<sup>[57]</sup> Copyright 2005, American Institute of Physics. b) Schematics of TTD. Reproduced with permission.<sup>[58]</sup> Copyright 2018, American Institute of Physics. c) Schematic representation of the optical measurement setup. Reproduced with permission.<sup>[58]</sup> Copyright 2021, American Association for the Advancement of Science.

basis,  $VO_2$ -based devices with excellent performance have been developed and put into the market. According to the existing research, the regulatory structure of  $VO_2$ -based devices can be roughly divided into planar structure, sandwich structure, FET structure, ionic liquid gating structure and some combinations of the above structures. Below we will introduce the characteristics and application development of  $VO_2$  E-MIT device regulatory structure.

*Planar Structure*:  $VO_2$  planar structure refers to the working electrodes of  $VO_2$  nanostructure in the device in the horizontal direction, and the size of the applied lateral electric field strength is controlled by adjusting the size of the test electrodes, the distance between the electrodes and other parameters, and most double-ended device structures belong to this structural category.

As early as 2005, Kim et al.<sup>[57]</sup> of the Daejeon Electronics and Telecommunications Research Institute in South Korea used laser ablations to deposit VO<sub>2</sub> film on Al<sub>2</sub>O<sub>3</sub> substrate, and prepared the device structure on the left of **Figure 6a**, when T = 35 °C, it was found that the current density of the film was abruptly changed, so it was pointed out that the electric field induced VO<sub>2</sub> MIT.

Afterwords, Gu et al.<sup>[58]</sup> prepared a two-terminal device (TTD) based on VO<sub>2</sub> polycrystalline thin film on quartz and Si/SiO2 substrates for direct current drive MIT experiments (Figure 6b), and found the dominant role of Joule heating mechanism in inducing VO<sub>2</sub> MIT. Unlike Gu et al, Sun et al.<sup>[59]</sup> coated a PEG/VO<sub>2</sub>(M) layer between two planar electrodes and achieved a sudden current transition at 40 V, demonstrating that the VO<sub>2</sub> phase transition can be controlled by a pure electric field. It can be seen that although the planar structure is simple, the mechanisms that induce the phase transition of VO<sub>2</sub> may be diverse,

and its performance is also easily affected by the preparation process and substrate type.

Based on this simple configuration, the planar structure is suitable for making traditional electric switches, which is convenient for studying the influence of Joule heating and other factors on phase transition and testing optical properties. For example, Valle et al.<sup>[5a]</sup> reported in "Science" the spatiotemporal characterization of VO<sub>2</sub> field-induced insulator-to-metal transition, in which the Au/Ti electrode defines a planar VO<sub>2</sub> bridge for inducing resistance switching (Figure 6c), measuring reflectivity, and investigating Joule heating.

In addition, some researchers have also adopted a 1D structure similar to the planar structure in the phase transition test of VO<sub>2</sub> nanowire structure.<sup>[5b,60]</sup> Compared with other field control structures, planar structures have the advantages of simple preparation, easy to test and observe current, and no obscuration in the VO<sub>2</sub> phase transition area, and have attracted more attention in the application of current/resistance switches and some optical switches. However, it is arduous to suppress the influence of Joule heating in a planar structure without adding an external cooling source, so the application of this structure has certain limitations.

Sandwich Structure: Sandwich structure is VO<sub>2</sub>-based electronic device structure made by stacking layers of material and inducing a VO<sub>2</sub> phase transition by applying a vertical electric field to the working electrode, such as the MOM and MIM structures mentioned in some literature. The sandwich structure used by Stefanovich et al. who first conducted systematic research on VO<sub>2</sub> E-MIT.The following is a brief introduction to the development of the sandwich structure:

In 2013, Zhou et al.<sup>[61]</sup> achieved ultrafast conversion of steep resistance with large switching ratio of  $VO_2$  film through the

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**Figure 7.** a) Schematic of the sandwich sample structure. Reproduced with permission.<sup>[62]</sup> Copyright 2015, American Institute of Physics. b) The typical device architecture and an atomic force microscope (AFM) image of the VO<sub>2</sub> channel area. S, D, and G indicate the source, drain and gate electrodes, respectively. Reproduced with permission.<sup>[63]</sup> Copyright 2015, NATURE RESEARCH. c) Schematic diagram and insulator-to-metal transition in three structures of MIM VO<sub>2</sub> devices with voltage sweep. Reproduced with permission.<sup>[64]</sup> Copyright 2021, WILEY-VCH.

electrode- $VO_2$ -electrode (MIM) two-terminal structure, and thus negated the simple Joule heating mechanism explanation for the  $VO_2$  phase transition.

To reduce the effects of Joule heating, Daichi Matsunami and Asaya Fujita<sup>[62]</sup> fabricated a layered structure like **Figure 7**a, in which the designed insulating layer acts to block Joule heating generation, and the electric field strength applied to VO<sub>2</sub> can also be changed by adjusting the thickness of the insulating layer. To further rule out the effects of Joule heating, Hao et al.<sup>[65]</sup> designed the FTO/VO<sub>2</sub>/FTO sandwich structure, and the device current jumps at T = 20 °C and V<sub>TH</sub> = 9.2 V, achieving non thermally controlled VO<sub>2</sub> phase transition.

Unlike the traditional overlapping sandwich structure, Kabir et al.<sup>[64]</sup> proposed three MIM structures based on VO<sub>2</sub> electrically triggered IMT: offset, no offset, and overlap (Figure 7c). Experimental and simulation results show that the electric field is the main factor inducing the VO<sub>2</sub> MIT, and the magnitude is only related to the structure, and there are differences in the resistive switching ratios of different structures, which is important for improving the scalability and reducing the power consumption of high-speed electronic devices. Compared with other test structures, the sandwich structure is easier to achieve large-area modulation of VO<sub>2</sub> phase transition by electric field, and trigger VO<sub>2</sub> MIT through a single field. In addition, due to the role of pure electric field mechanism, it is easier to achieve ultrafast switching of VO<sub>2</sub> devices using the sandwich structure, and the sandwich structure is small in size and easy to integrate, which is attractive in the new generation of optical and electrical devices.

*FET Structure*: After discovering the special E-MIT mechanism of  $VO_2$ , some researchers linked it to the working mecha-

nism of FETs, and tried to use gate voltage to trigger  $VO_2$  resistance switches to realize the gating function of FETs.

In 2004, Kim et al.<sup>[10a]</sup> designed a three-terminal FET device and tested circuit, using the source drain field and gate field to induce holes to the conduction band, triggering VO<sub>2</sub> MIT, and initially realized the function of Mott FET. Kim's work opened up the study of VO<sub>2</sub>-base FET structures.

In recent year, In recent years, researchers have designed many novel FET structures using VO<sub>2</sub>. For example, Sasaki et al.<sup>[63]</sup> demonstrated the reversible and dramatic regulation of vanadium dioxide nanowire transition properties by electric field-induced hydrogenation at room temperature using fieldeffect transistors (PG-FETs) with planar gates (Figure 7b), where nanogaps can be used to modulate the atmosphere in which VO<sub>2</sub> nanowires are located, similar to planar structures. Afterwards, Abbas et al.<sup>[66]</sup> studied the effect of electric fields on VO<sub>2</sub> backgate field-effect transistor (FET) device, achieving a two-order modulation of VO<sub>2</sub> resistance at a gate voltage of 80 V.

Similarly, Yajima et al.<sup>[67]</sup> also designed a backgate FET structure based on VO<sub>2</sub>, using Nb:TiO<sub>2</sub> as the dielectric layer, the pinch effect of  $I_D$  saturation in the phase transition device was observed for the first time, and the effect of drain voltage sharpening gated leakage current transition was found.

Compared with two-terminal devices,  $VO_2$ -based FET devices have reversible and non-volatile response at room temperature, and the threshold voltage is lower, which has advantages in the design and manufacture of some electronic components such as Mott FETs and non-volatile memory, low-voltage switches, and neuromorphic devices. However, most of the structures use electrostatic gating methods, which have high requirements for www.advancedsciencenews.com

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**Figure 8.** a) The transistor geometry of Li-doing by bias voltage. b) The  $I_{SD}$ - $V_G$  comparison for  $VO_2/TiO2(001)$ ,  $VO_2/TiO2(100)$ , and  $VO_2/TiO_2(110)$ . Reproduced with permission.<sup>[68]</sup> Copyright 2018, Elsevier. c) Ionic liquid gating structure and hydrogen ion movement in  $VO_2$  device, and reversible phase transition of  $VO_2$  by tuning hydrogenating level through gating. Reproduced with permission.<sup>[69]</sup> Copyright 2019, American Association for the Advancement of Science.

dielectric constant, thin film quality and gating field, resulting in high difficulty in the preparation of devices Ionic liquid gating structure.

*Ionic Liquid Gating Structure*: Unlike ordinary FETs, ionicliquid gated structures use ionic liquids as a dielectric region to control ion migration through an electric field to induce VO<sub>2</sub> phase transition. Among them, the electric double-layer transistor (EDLT) structure is the most classic.

In 2012, Liu et al.<sup>[12b]</sup> constructed an electric double-layer transistor (EDLT) to accumulate electrolyte-VO<sub>2</sub> surface charge to trigger the surface metal-insulator transition (SMIT) on the surface of single-crystal VO<sub>2</sub> nanobeams by electrostatic injection. In the same year, Nakano's group<sup>[5c]</sup> reported in "Nature" a VO<sub>2</sub>-based electric double-layer transistor (EDLT), using organic ionic liquid DEME-TFSI as the gate region medium, to study the electrochromic behavior of the device, showing the multifunctional application value of VO<sub>2</sub>-EDLT.

The choice of dielectric layer material is critical to device performance, and in recent years, several researchers have achieved excellent device performance using highly efficient electrolyte materials. Chen et al.<sup>[68]</sup> of the University of Science and Technology of China selected a water-free electrolyte gel Li<sup>+</sup>/propylene carbonate as the IL dielectric layer (**Figure 8a**), and realized the phase modulation of nano-VO<sub>2</sub> crystal thin film under the gated threshold voltage  $V_G = 2 V$  (Figure 8b). Zou et al.<sup>[69]</sup> dissolved NaClO<sub>4</sub> in PEO to configure a gel-like electrolyte and act as an IL layer, as shown in the Figure 8c, by adjusting hydrogen ion doping by electric field gating to achieve light transmittance modulation of smart windows. Smieszek et al.<sup>[12a]</sup> studied the phase transition dynamics of the two-dimensional VO<sub>2</sub> layer under high

electron injection limits, and realized the  $VO_2$  phase transition by electrochemical gating, in which the ionic liquid uses a propylene acid (PC) electrolyte containing Li<sup>+</sup> or TBA<sup>+</sup> perchlorate.

Compared with other structures, ionic liquid gating can inject more carriers, which proposes a new way for electric field induction and ion migration, and this control method has great application prospects in  $VO_2$ -based electrochromic devices such as smart windows and filters. However, in some electronic devices, ionic liquids may induce electrochemical reactions at the solid-liquid interface at the same time, making precise control difficult and limiting the study of electrical phase control.<sup>[67]</sup>

In recent years, research information on the modulation of VO<sub>2</sub>-based devices is summarized in **Table 1**. At present, the research of device structure mainly focuses on how to achieve ultrafast phase transition of VO<sub>2</sub>, avoid Joule heating, reduce control difficulty and improve control accuracy, etc., in addition, the device structure has a significant impact on the phase transition induction mechanism of VO<sub>2</sub> under electric field. Therefore, studying the structure of VO<sub>2</sub>-based devices is of great significance to the exploration of the mechanism of controlling VO<sub>2</sub> phase transition in the future and the new generation of optical and electrical devices.

## 4.2.2. Modulation Mechanisms

In the design of  $VO_2$ -based devices, the choice of  $VO_2$  MIT regulation mechanism is particularly important, which is greatly related to the response characteristics and application direction

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Table 1	. The structure and	l mechanism	of electric fiel	d controlled VO	2 MIT in recent	vears
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Date	Modulation structure	V <sub>TH</sub> (RT) <sup>a)</sup>	Modulation mechanism	Reference.
2018	Ionic liquid gating	2۷	Electrochemical mechanisms (Li+)	[68]
2018	Planar	40V	Joule Heating	[58]
2018	Tip electric field	-2.4 V	Oxygen vacancies	[70]
2018	Planar	0.4 V or	Landau-Zener tunnel breakdown	[71]
		2.87×10 <sup>7</sup> V m <sup>-1</sup>		
2019	Ionic liquid gating	1.0 V	Electrochemical mechanisms(H+)	[69]
2019	Ionic liquid gating	1.2 V	Electrochemical mechanisms(H+)	[11b]
2020	Nanobeam	$\approx$ 5.2 V or	Electric field	[5b]
		1.5 MV m <sup>-1</sup>		
		(Teir = 105 K)		
2020	Planar	38 V or	Joule heating and Electric field	[72]
		10 <sup>5</sup> V m <sup>-1</sup>		
2021	Planar	15.7 V or	Joule heating and Electric field	[73]
	(Interdigitated Electrodes)	$pprox 10^6 \text{ V m}^{-1}$		
2021	Planar	10 V	Joule Heating	[5a]
		(Teir = 335 K)		
2021	Sandwich	5 V or	Pool-Frenkel Mechanism	[64]
		1.57×10 <sup>7</sup> V m <sup>-1</sup>		
2022	Tip electric field	0.5 V–1 V	Oxygen vacancies	[74]
		(Vbias>4 V)		

<sup>a)</sup> RT is room temperature.

of the device. For two decades, scientists have proposed a variety of division concepts for the mechanisms of VO<sub>2</sub> electric induced phase transition, and early in the research, researchers focused on studying the effects of Joule heating in VO<sub>2</sub> E-MIT to determine whether VO<sub>2</sub> phase transition can be induced by pure electric field. With the study of microscopic processes and advances in detection techniques, multiple E-MIT mechanisms have been reported.<sup>[5b,21,64,72,75]</sup> The following paper mainly discusses the regulatory mechanism of VO<sub>2</sub>-based devices from the Joule heating, electric field mechanism and electrochemical mechanism.

*Joule Heating*: Joule heating effect is the most classical mechanism for regulating  $VO_2$  phase transition, which comes from current heating in  $VO_2$  electronic devices and is the research focus of  $VO_2$ -based electronic devices. The following is a brief description of the development of the Joule heating mechanism in  $VO_2$  phase transition.

Bae et al.<sup>[9]</sup> fabricated a two-terminal memristor memory based on a single VO<sub>2</sub> nanowire, which realized the resistance switching and reseting through the self-joule heating effect under bias voltage. Subsequently, Rathi et al.<sup>[76]</sup> identified five current transition stages of the I-V curve of VO<sub>2</sub> NB at -4+4 V, and the study showed that Joule heating and the Poole-Frenkel mechanism play a role in different stages of VO<sub>2</sub> phase transition.

Wang et al.<sup>[72]</sup> applied voltage to the film, they found that electric field mechanism and Joule heating coexist, and these two factors have a synergistic effect, which can reduce the requirements of a single factor to trigger the phase transition, in addition, Wang and his team believe that after de-voltage, Joule heating can maintain the tetragonal rutile structure of VO<sub>2</sub> film for a period of time.

In 2021, Bayram et al.<sup>[73]</sup> used COMSOL to perform finite element simulation analysis of their VO<sub>2</sub>-based suspended membranes modulator, and the results showed that the phase transition observed in the experiment was caused by Joule heating and electric field. In the same year, Valle et al.<sup>[5a]</sup> studied the spatiotemporal characteristics of the transition from field-induced insulator to metal and finally concluded that the growth of the metallic phase can be explained by Joule heating alone, and Joule heat dominates the growth of the metallic phase region when the structural current increases. Research by Valle et al.<sup>[5a]</sup> identified key parameters that control switching speed, which are critical for proper material selection and device design in emerging information technologies such as optoelectronics and neuromorphic computing.

On the one hand, the existence of Joule heating mechanism can achieve superior modulation effect and new application of devices by cooperating with electric fields, and on the other hand, it also provides a new development direction for VO<sub>2</sub> thermochromic applications. However, due to the existence of Joule heating, the sensitivity, response speed, control accuracy and energy consumption of some optical and electrical devices are affected, so how to suppress the influence of Joule heating has become the research focus of VO<sub>2</sub>-based devices. Pure electric field triggering methods such as carrier injection or increasing carrier density are positive choices for VO<sub>2</sub> device start-up that suppresses the influence of Joule heating.

*Pure Electric Field*: As early as 2000, experiments by Stefanovich et al.<sup>[13b]</sup> showed that electron injection can trigger VO<sub>2</sub> MIT. As the most representative regulation method under the electric field mechanism, carrier injection has been widely studied and applied, especially in the field of ultrafast electronic devices, and has become an ideal trigger mechanism.

In 2004, Kim et al.<sup>[10a]</sup> induced MIT by gate injection holes in a three-terminal device, revealing that MIT relies on hole carriers in semiconductor systems, and proposed that hole carrier injection causes the  $I_{DS}$ - $E_{DS}$  curve of the device to shift. Pergament et al.<sup>[77]</sup> claim that high electric fields can be injected into carriers through contact, resulting in an increase in carrier concentration, and according to Mott's criterion, MIT is induced when the carrier concentration reaches a critical concentration.

In 2017, Sohn et al.<sup>[10b]</sup> found that negative differential resistance (NDR) occurs at an approximately constant current level, noting that this is the result of carrier injection-induced phase transitions, independent of thermally induced phase transitions. In addition, some studies have shown that the Pool-Frenkel effect under pure electric field can effectively reduce the energy barrier, excite free electrons, and increase carrier concentration.<sup>[5b,12b,64,78]</sup> Zener tunneling<sup>[5b]</sup> is also a well-studied mechanism of field-induced doping and Mott instability in insulators.

There is no uniform answer to the way and explanation of VO<sub>2</sub> phase transition under the pure electric field mechanism, which can be determined according to the specific structure and working mode of the device. However, the more unified view is that the pure electric field mechanism is easier to achieve the ultrafast phase transition of VO<sub>2</sub>, and the energy consumption is lower due to the small influence of Joule heating, which is extremely promising in the integration of electronic devices. At present, for the development of VO<sub>2</sub> devices, such as new FETs, light detectors, neural networks and other high-speed optical and electrical applications, the electric field mechanism is often the trigger mechanism that is the primary consideration.

*Electrochemical Effect*: The electrochemical mechanism is based on the electric field as the intermediary, through ion migration, bonding or splitting that occurs through chemical bonds, and then change the  $VO_2$  lattice structure or electron correlation to achieve  $VO_2$  modification. The two most common forms of electrochemical mechanisms are ion doping and oxygen vacancy. Both forms are often involved in liquid-gating structures.

The most common ion doping is H<sup>+</sup> and Li<sup>+</sup> doping. In 2019, Deng et al.<sup>[11b]</sup> used gate injection H<sup>+</sup> to combine with O<sup>-</sup> to form H-O bonds (**Figure 9**a), increasing carrier density, making electron-electron and electron-structure correlation stronger in VO<sub>2</sub>, resulting in shortening of V-V chain length, thereby inducing VO<sub>2</sub> phase transition. In 2022, Smieszek et al.<sup>[12a]</sup> designed an electrochemically gated structure to form a Li–O bond at O<sup>2-</sup> by injecting Li<sup>+</sup> into an ionic liquid, increasing carrier density and inducing VO<sub>2</sub> phase transition.

Finally, the oxygen vacancing mechanism is also a common electrochemical mechanism. The principle is that oxygen migration occurs in VO<sub>2</sub> through voltage bias, vacuum high-temperature annealing, etc., resulting in the formation of oxygen vacancies, which make VO<sub>2</sub> take on metallic properties through structural or electron-related effects, in recent years the research on oxygen vacancies mechanism is relatively hot.

In 2016, Chen et al.<sup>[11a]</sup> used EMIM-BF4 ionic liquids for ionic liquid gating experiments, as shown in the Figure 9b, under the control of gating voltage, oxygen ions in VO<sub>2</sub> were captured by EMIM+, resulting in oxygen vacancies in VO<sub>2</sub> films. On the one hand, the occurrence of oxygen vacancies will cause lattice relaxation and promote the deformation of VO<sub>2</sub> monoclinic phase to rutile phase. On the other hand, the defect and the adjacent V atom produce a polarized charge, resulting in an increase in the Fermi energy level, and VO<sub>2</sub> shows metallic properties. Sharma et al.<sup>[70]</sup> found that the chemical potential and conductivity of the local VO2 surface were altered by applying voltage of different polarities at the tip of scanning probe microscopy (SPM) to adjust oxygen stoichiometry, and Y. Sharma's work highlighted the importance of oxygen vacancies in VO<sub>2</sub> MIT. Zhang et al.<sup>[74]</sup> generated oxygen vacancies by reacting hydrated hydrogen ions with oxygen ions in VO<sub>2</sub> based on modulation by tip bias modulation. The more oxygen vacancies generated, the higher the temporal stability of the modulation, which is critical for VO<sub>2</sub>-based devices.

The application of field-controlled oxygen vacancy mechanism opens up a new control method for VO<sub>2</sub> devices, which is of great significance to the development of ionic electronic devices, making nanoscale electrochemical control of optical and electrical devices feasible, and based on oxygen vacancy characteristics, VO<sub>2</sub> materials can be used for long-term storage, which has great application potential in the field of non-volatile device.

In Table 1, the phase transition mechanism involved in the research of VO<sub>2</sub>-based devices in recent years is summarized. In recent years, the application of VO<sub>2</sub> material field-induced phase transition involves a diversified mechanism, the most common of which is the combination of electric field mechanism and Joule heating mechanism, some studies use electric field to trigger phase transition, Joule heat to maintain the metal phase,<sup>[72]</sup> or use electric field to maintain VO<sub>2</sub> phase in the hysteresis region, with Joule heating to induce two-phase transition.<sup>[9]</sup> In addition, the fusion of hydrogen doping and oxygen vacancies in electrochemical mechanisms has also been reported in recent years.<sup>[79]</sup> Studying the VO<sub>2</sub> trigger mechanism and regulation means can better understand the VO<sub>2</sub> phase transition mechanism, which is of great significance for the future development of VO<sub>2</sub> applications and the design of a new generation of optical and electrical devices.







**Figure 9.** a) Structural evolution of VO<sub>2</sub> (M) with proton doping predicted by DFT calculations. Reproduced with permission.<sup>[11b]</sup> Copyright 2019, WILEY-VCH. b) The scheme for the ion liquid gating film devices. Reproduced with permission.<sup>[11a]</sup> Copyright 2016, WILEY-VCH.

## 4.2.3. E-MIT Modulation Advantages

Controlling VO<sub>2</sub> phase transition through external electric field is a classic control method for VO<sub>2</sub>-based devices, and the obvious control advantages make E-MIT widely used in the field of electronic devices. First of all, E-MIT, as an electronically controlled way to trigger the VO<sub>2</sub> phase transition, means that VO<sub>2</sub> materials have application possibilities in the field of electronic devices. At the same time, E-MIT makes it possible to miniaturize and integrate VO<sub>2</sub>-based electrical components.

Second, E-MIT control method is more convenient and practical. For example, when designing the structure of miniature electronic devices such as switches, memristors, and filters, it is obviously not ideal to use external source heating to realize the function of the device and put it into use, and E-MIT highlights the strong environmental matching. In addition, based on this, VO<sub>2</sub> E-MIT devices consume less energy, which is attractive in optical and electrical device design and application.

Finally, the most obvious advantage of E-MIT is the phase transition speed, and in the E-MIT study, the researchers found that ultrafast E-MIT can be achieved under the control of an external electric field. In 2013, Zhou et al.<sup>[61]</sup> used the VO<sub>2</sub> MIM voltage control structure to achieve a device switching time of less than 2 ns, pointing out that VO<sub>2</sub> phase transition is triggered faster by carrier injection than heating, which is consistent with Xiong et al.  $^{[80]}$  that Joule heating affects  $\rm VO_2$  ultrafast phase transition.

In 2014, Rathi et al.<sup>[76]</sup> demonstrated the principle of the Poole-Frenkel effect using a square wave voltage pulse with a duration of 1 µs, and tested that the switching time of the VO<sub>2</sub> NB structure is ≈100 ns. Xue et al.<sup>[81]</sup> achieved a fast switching speed of 17 ns by using 1D vanadium dioxide nanochannels constructed by electric field-induced ion migration in the MIM structure of V<sub>2</sub>O<sub>5</sub>.

In 2021, Valle et al.<sup>[5a]</sup> reported in "Science" that the VO<sub>2</sub> film they made metallized in a scale of  $\approx 10^{-7}$ s, and then expanded at a slower rate to the final filament structure.

Compared with electric field induction, electronic devices using thermally induced phase transition mechanism cannot achieve high device switching speeds, such as some Si-VO<sub>2</sub> optical modulators with switching times as long as  $25\mu$ s, due to the use of thermally induced phase transition to slow down the switching time.<sup>[82]</sup> For example, Bayram et al.<sup>[73]</sup> designed a VO<sub>2</sub>based near-infrared modulator that directly applies a pulse voltage on the VO<sub>2</sub> layer to trigger the IMT, achieving a near-infrared modulation speed of sub-milliseconds, but they say that due to the influence of Joule heating, the response speed of the device is still limited. The response speed of VO<sub>2</sub>-based electronic devices or the switching time of related devices is even lower than the ns level, which is attractive for the research of ultrafast electronic devices, so the phase transition time has always been the research focus of VO<sub>2</sub>-based electronic devices.

## 4.3. Optical Modulation

In addition to temperature and external electric field regulation of VO<sub>2</sub>, optical regulation is also a common trigger method to control the phase transition of VO<sub>2</sub>. In 1971, Roach and Balberg<sup>[83]</sup> made the first attempt to measure the switching speed of optical induced phase transition in VO<sub>2</sub>, and successfully induced the phase transition of VO<sub>2</sub> sputtering film within 20 ns using a continuous wave He-Ne laser to detect it. The study of optical modulation VO<sub>2</sub> phase transition has been carried out for a long time, which has opened up a new research field for VO<sub>2</sub>-based optical devices.

The research on the phase transition induced by light in VO<sub>2</sub> system, the VO<sub>2</sub> phototriggered phase transition system and the phase transition mechanism are the focus concerned by researchers. Like the phase transition of VO<sub>2</sub> induced by external electric fields, the photo-induced phase transition (P-MIT) of VO<sub>2</sub> also has thermal and non-thermal mechanism explanations (electrons, phonons, lattice, etc.). The following will discuss the development of VO<sub>2</sub> P-MIT in recent years from two aspects: VO<sub>2</sub> P-MIT test system and mechanism.

#### 4.3.1. Optical Modulation Systems

In studying photo-modulated VO<sub>2</sub> MIT, the researchers used different trigger lasers and detection lasers to build test systems to explore the phase transition of VO<sub>2</sub> induced by lasers. In 2001, Cavalleri et al.<sup>[84]</sup> studied the femtosecond structural dynamics of photo-induced VO<sub>2</sub> ultrafast solid-solid phase transition with femtosecond X-ray and visible pulse system for the first time, and realized the optical pump-induced VO<sub>2</sub> phase transition in only 100 fs, demonstrating the great potential of photoinduction in VO<sub>2</sub>-based ultrafast electronic devices. After that, researchers mostly used ultrafast lasers as the pump source of the optical trigger system to excite the VO<sub>2</sub> phase transition, and used the optical pump with lower energy as the detection light to detect the phase transition, and in recent years, reports on the VO<sub>2</sub> photoinduced phase transition test system have emerged endlessly.

In general, the all-optical test idea of using light to excite the phase transition and then using light to test the phase transition properties is a more traditional design concept of the VO<sub>2</sub> P-MIT test system. In 2018, the Zhai team of the University of Science and Technology of China<sup>[85]</sup> performed kinetic terahertz wave absorption measurement (KITA) on VO<sub>2</sub> nanofilms excited by 800 nm laser (as shown in the **Figure 10a**), quantitatively distinguished the dynamic response of photothermal excitation on the second timescale and the photodoping on the ps-ns timescale from the light-induced MIT, and determined the competing interactions between the two photo responses.

Wang et al.<sup>[86]</sup> used a homemade variable temperature Z-scanning device (as shown in the Figure 10b), in which the excitation laser source is a 380 fs pulsed laser at 1040 nm, and the beam is focused with a 150 mm focusing lens, and the radius of

the beam at the focusing is  $\approx$ 44.2 µm. They found that under different frequency laser excitation, the transmittance of samples in the +Z and -Z directions showed a trend of first sudden decrease and then slow increase, indicating that the P-MIT in the test is a typical laser thermal accumulation-induced phase transition process.

Different from the test ideas mentioned above, it is also an efficient test scheme to use light to excite the phase transition and then test the changes in the electrical properties of  $VO_2$  structures.

For example, Wei et al.<sup>[29a]</sup> of Beihang University fabricated a phase change anisotropic magnetoresistance device (PCAMR) (as shown in Figure 10c), in which VO<sub>2</sub> samples were made into Hall rods, and VO<sub>2</sub> MIT was induced by 660 nm light and magnetic fields to study magnetic and transmission characteristics through magnetoresistive measurements. During the test, they found that changing the size of the light field or magnetic field can change the size of the Hall rod resistance, so they thought that both the light field and the magnetic field could trigger the VO<sub>2</sub> phase transition, so that the device has light-controlled PCAMR characteristics.

In 2022, Li et al.<sup>[7a]</sup> designed a three-terminal test structure (as shown in Figure 10d) to measure the drain current change by using 64 mW cm<sup>-2</sup> red, green, blue, and ultraviolet pump light to excite VO<sub>2</sub> phase transition. The experimental results show that under ultraviolet light irradiation of 375 nm, the drain current I<sub>D</sub> has a significant jump, and the study shows that the photo-induced phase transition of VO<sub>2</sub> has a greater relationship with the wavelength of light.

**Table 2** summarizes the main parameters of the system built by researchers in recent years for VO<sub>2</sub> P-MIT testing. With the rapid development of femtosecond lasers, the construction of VO<sub>2</sub> P-MIT excitation system has also been more perfect, and femtosecond lasers have basically become the first choice for studying the pump source of VO<sub>2</sub> photo-induced phase transition trigger system. Studying the excitation method and system setup of VO<sub>2</sub> P-MIT can explore the triggering characteristics and physical properties of VO<sub>2</sub> photo-induced phase transition, which is of great significance to the application of VO<sub>2</sub> P-MIT all-optical devices. In subsequent research, how to adopt a more efficient pump excitation method has become the key to VO<sub>2</sub> P-MIT, and second, how to introduce VO<sub>2</sub> P-MIT characteristics into the application field of optical devices is also a major research topic.

#### 4.3.2. Optical Modulation Mechanisms

Similar to E-MIT, there is no unified mechanism explanation for the VO<sub>2</sub> P-MIT trigger mechanism, the mainstream debate is that the essence of VO<sub>2</sub> P-MIT is thermal excitation or laserinduced electron-lattice action to trigger VO<sub>2</sub> phase transition or both, for this, researchers have done a lot of works, achieved certain theoretical analysis results, the following will mainly discuss the development of VO<sub>2</sub> P-MIT mechanisms from the two separate and synergistic.

*Photo-Thermal Effect:* The mainstream explanation of the current thermal mechanism of  $VO_2$  P-MIT is that the laser irradiates the surface of the  $VO_2$  structure, and the energy of the laser is transferred to the  $VO_2$  lattice by causing the carrier







**Figure 10.** a) The schematic of KITA for photothermal induced VO<sub>2</sub> MIT. Reproduced with permission.<sup>[85]</sup> Copyright 2018, OPTICAL SOC AMER. b) Schematic of the variable temperature Z-scan setup. Reproduced with permission.<sup>[86]</sup> Copyright 2022, OPTICAL SOC AMER. c) Schematic drawing of the PCAMR device. Reproduced with permission.<sup>[29a]</sup> Copyright 2020, WILEY-VCH. d) Schematic illustration of the neuromorphic transistor stimulated using 375 nm UV light. The VO<sub>2</sub> film serves as a channel between the source (S) and drain (D) electrodes, and ionic liquid is used as a gating medium. Reproduced with permission.<sup>[7a]</sup> Copyright 2022, Springer Nature.

Table 2. Phase transition mechanisms of photoexcited VO<sub>2</sub> and parameters of excitation system.

Date	Wavelength	Repetition frequency	Pulse width	Mechanisms	Energy density	Reference.
2018	800 nm	500 Hz	130 fs	Joule heating	15 mJ cm <sup>-2</sup>	[87]
2018	800 nm	1 kHz	40 fs	Photothermal Effect and 9 mJ cm <sup>-2</sup> Photodoping		[85]
2020	400 nm	1 kHz	150 fs	Lattice Strain	22 μJ cm <sup>-2</sup>	[88]
2020	1028 nm	5 kHz	170 fs	Tensile Strain 0.7 mJ cm <sup>-2</sup>		[89]
2020	660 nm	N/A	N/A	Interfacial Strain Coupling	$0.5 \text{ W cm}^{-2}$	[29a]
2021	1023 <u>±</u> 8 nm	N/A	280 fs	Heterogeneous Nucleation	2 mJ cm <sup>-2</sup>	[90]
2022	375 nm	N/A	N/A	Oxygen vacancies	64 mW cm <sup>-2</sup>	[7a]
2022	1040 nm	100 kHz	380 fs	Accumulation of Thermal Effects	0.04 mJ cm <sup>-2</sup>	[86]

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concentration to change, resulting in an increase in the temperature of the energy absorption region, which in turn triggers the VO<sub>2</sub> phase transition.

Lin et al.<sup>[91]</sup> selected a 308 nm excimer laser to irradiate VO<sub>2</sub> samples at different energy, and found that under a certain degree of irradiation, the morphology and optical properties of VO<sub>2</sub> film changed significantly, which proved that the phase transition of VO<sub>2</sub> induced by laser was caused by thermal effects. Scherbakov et al.<sup>[92]</sup> filled the opal with VO<sub>2</sub>, and used the YAG:Nd laser second harmonic pulse at room temperature to excite VO<sub>2</sub> to generate free carriers, and after relaxation heating, VO<sub>2</sub> underwent a phase transition, resulting in spectral blue shift.

In 2022, Wang et al.<sup>[86]</sup> studied fs laser-induced changes in optical properties of VO<sub>2</sub> films with variable temperature Z-scanning. Through the 100 kHz temperature change experiment, it is found that the modulation depth of the laser-induced VO<sub>2</sub> phase transition is consistent with the modulation depth of the ambient temperature-induced phase transition, and increases linearly with the thickness, which further confirms that the phase transition is caused by the accumulation of high repetition frequency laser thermal effects.

The photothermal effect is the most intuitive theoretical explanation of VO<sub>2</sub> P-MIT, which is a fundamental thermally triggered phase transition, which is of great significance in the theoretical study of phase transition of VO<sub>2</sub> materials. However, because of the existence of thermal effects, the energy consumption is high and the control accuracy is poor, which limits its application in optical/electrical devices.

*Electron Effect and Lattice Strain*: In addition to the traditional photo-thermal effect to induce  $VO_2$  phase transition, scientists have found in long-term experiments that  $VO_2$  phase transition can be achieved by non-thermal laser-induced electron-lattice action, breaking through the original limitation that  $VO_2$  phase transition are triggered by heating. The so-called photoelectron-lattice effect refers to the phase transition of  $VO_2$  materials by releasing electrons to occupy the electron orbital or cause lattice space change under laser induction.

In 2004, Liu and others at the University of Puerto  $\text{Rico}^{[93]}$ first reported the maximum polarizability observed in VO<sub>2</sub> films and the lattice dynamics process related to excited states, in which the research process used the degenerate four-wave hybrid (DFWM) measurement method for transient holographic imaging, found the polarizability change caused by lattice change, and pointed out that the transient lattice distortion triggered structural changes, affirming the explanation of the non-thermal lattice mechanism of VO<sub>2</sub> P-MIT.

Mogunov et al.<sup>[89]</sup> reported that the epitaxial layer of vanadium dioxide generated picosecond strain pulses under femtosecond photo-excitation, and found that photo-induced first-order phase transition (PIPT) contributes up to 45% to the ultrafast expansion of VO<sub>2</sub> materials, much higher than the contribution of thermoelasticity to material expansion, so a non-thermal mechanism for generating picosecond strain pulses by ultrafast light-induced first-order phase transition (PIPT) is proposed.

In 2022, Li et al.<sup>[7a]</sup> reported a photo-induced non-volatile VO<sub>2</sub> phase transition neuromorphic ultraviolet sensor, discovered the generation of photo-induced oxygen vacancies, and elaborated this P-MIT oxygen vacancy mechanism: the photon energy

(3.35 eV) of 375 nm ultraviolet excitation light is greater than the activation energy of generating oxygen vacancies (3–3.5 eV), so oxygen can be released from VO<sub>2</sub> films in a hypoxic environment, thereby generating oxygen vacancies in the crystal lattice. As oxygen vacancies appear, V atoms lose some electrons and release them into the neighboring V-3d state, which partially occupy the  $d_{//}$  orbital and  $\pi^*$  orbital, resulting in an electron phase transition. In addition, the difference in the radius of V ions caused by oxygen vacancies in the lattice and electron release also leads to the strain of VO<sub>2</sub>, which changed from a low-symmetric monoclinic phase to a highly symmetric rutile phase and further induced a metallic phase.

In recent years, non-thermo-photogenic phase transition of VO<sub>2</sub> system has become the focus of VO<sub>2</sub> P-MIT research, and compared with the phase transition caused by photo-thermal, the former has obvious application advantages in device response speed and control accuracy, which is particularly important in the development of all-optical devices. In addition, the study of VO<sub>2</sub> non-thermo-photo-induced phase transition plays a significant role in exploring the deep mechanism of material phase transition and the strong correlation between VO<sub>2</sub> electrons and electrons, which is exceedingly beneficial to the study of VO<sub>2</sub> condensed matter physics.

*Cooperative interaction*: As VO<sub>2</sub> P-MIT research advances, the researchers found that the mechanism of VO<sub>2</sub> photoinduced phase transition may not be single, but a synergistic effect of thermal and non-thermal mechanisms. In 2006, Liu's team<sup>[94]</sup> observed the photo-induced ultrafast nonlinear optical response in the optical measurement of VO<sub>2</sub> films, found that there was a slow change process after the transient response, and proposed for the first time that the excitoncontrolled VO<sub>2</sub> phase transition model included ultrafast tunneling and thermal induction after exciton recombination in VO<sub>2</sub> system.

Zhai et al.<sup>[85]</sup> used femtosecond laser-driven kinetic terahertz wave absorption to quantitatively separate the slow photothermal response and the ultrafast photo-doping response on the time scale from seconds to picoseconds, and found that they competed with each other: the amplitude of the photo-doping response was enhanced at low photo-thermal accumulation, while the amplitude of the photo-doping response was suppressed when the high photo-thermal accumulation reached 60%. In addition, it is found that the photo-induced heating accumulation in the film significantly reduces the pump threshold of photodoping-induced phase transition, and the experimental results of Zhai et al. have a guiding effect on the studies of VO<sub>2</sub> photothermal and non-photothermal triggering.

In fact, whether it is thermal trigger or non-thermal trigger, the trigger mechanism is fundamentally photo-excited electrons, so the study of VO<sub>2</sub> photo-induced phase transition process can more clearly demonstrate the microscopic process of its phase transition. In the future, the research of collaborative triggering mechanism is still the focus of VO<sub>2</sub> photo-induced phase transition research, only by clearly understanding the deep trigger mechanism of VO<sub>2</sub> photo-induced phase transition can we better avoid the influence of adverse factors in the design of related optical devices, especially all-optical devices, and maximize the performance of the device.

## 4.3.3. P-MIT Modulation Advantages

 $VO_2$  P-MIT, as a special material phase transition modulation method, has been attracting much attention in the field of optics. The biggest difference between optical triggering and other triggering methods is that optical triggering chooses to trigger  $VO_2$  phase transition in light-controlled mode, which is intensely attractive in new optical devices, which is also the first prerequisite for application in all-optical devices. In addition, the relevant studies of  $VO_2$  photo-induced phase transition show that  $VO_2$  ultrafast phase transition can be easily achieved by using ultrafast lasers, which has obvious response speed advantages over general E-MIT.

According to the light control system designed in recent years summarized in Table 2, it can be seen that how to reduce the energy density of the excitation pump source and reduce the design difficulty of the photo-triggered system is the focus of future research on the application of  $VO_2$  photo-induced phase transition. Although the phase transition of  $VO_2$  under photo-excitation is fast and can be completed in sub-picoseconds, its recovery time is relatively long. Zhang et al.<sup>[95]</sup> found that the long recovery time of  $VO_2$  phase transition under photo-excitation is caused by the heat dissipation and relaxation of photo-carriers.

In the future, a new generation of optical devices will gradually develop toward refinement and miniaturization, and the requirements for control conditions will be more demanding. With the development of optical communication and optical transmission components in recent years, optical control is expected to become a more efficient alternative to optical and electrical control after electronic control, especially in the field of integrated optical path systems and chip manufacturing. VO<sub>2</sub> materials with excellent all-optical properties have naturally become popular research materials for the next generation of all-optical devices.

#### 4.4. Strain Engineering Modulation

As we all know, VO<sub>2</sub> phase transition is closely related to its lattice configuration change, so some scientists have tried to promote the lattice change through stress engineering to achieve the purpose of triggering phase transition or reducing  $T_C$ . At present, there are two modulation methods for VO<sub>2</sub> phase transition in strain engineering, one is the interfacial strain modulation caused by the internal lattice mismatch, and the other is the external macrostrain modulation due to applied mechanical deformation (bending, stretching, compression, twisting, etc.).<sup>[96]</sup> This chapter mainly describes and summarizes the current research status of VO<sub>2</sub> strain engineering from the stain engineering methods and mechanisms of VO<sub>2</sub> phase transition modulation.

## 4.4.1. Strain Engineering Modulation Methods

*Interfacial Strain*: Film structure is the most common application form of  $VO_2$ , based on the principle of interfacial strain caused by lattice mismatch of materials at the contact surface of  $VO_2$  film and other materials, some examines can adjust the

phase transition temperature of VO<sub>2</sub> film and the optical and electrical properties before and after phase change by selecting different film substrates or surface contact materials or adjusting VO<sub>2</sub> film thickness. The following is a brief timeline to briefly describe the interfacial strain studies on VO<sub>2</sub> film structure in recent years.

In 2018, Ren et al.<sup>[97]</sup> performed "film increase" and "film reduction" operations on VO<sub>2</sub> films deposited on TiO<sub>2</sub> substrates through "bottom-up" epitaxial growth and "top-down" chemical etching, and based on the interfacial strain effect at the VO<sub>2</sub>/TiO<sub>2</sub> interface, the opposite T<sub>C</sub>-film thickness change phenomenon was discovered, and a new interfacial strain modulation scheme based on film thickness was realized.

Afterwards, Sang et al.<sup>[18d]</sup> prepared a series of high-quality  $VO_2/Al_2O_3$  films by magnetron sputtering, as shown in the **Figure 11**a, the interface height mismatch between the  $VO_2$  film and the  $Al_2O_3$  substrate led to the interfacial strain of the  $VO_2$  film, and through experiments, it was found that the phase transition temperature of the  $VO_2$  film was significantly lower than 68 °C.

In 2022, Azad et al. in the United States<sup>[3b]</sup> studied the interfacial strain of VO<sub>2</sub> deposited on six substrates: c-plane, Sapphire, SiO<sub>2</sub>/Si, AT-Cut Quartz, GaN/AlGaN/GaN/Si and Muscovite, and found that there were differences in the transition temperature of VO<sub>2</sub> electrical properties, the transition temperature of 1500 nm optical transmission and XRD spectrum on different substrates, which indicated that different lattice constants have different interfacial strains. The conclusion of Azad et al. further points out that substrate selection has great modulation potential for interfacial strain.

The manipulation of interfacial strain  $T_{MIT}$  caused by lattice mismatch between VO<sub>2</sub> film and buffer layer or substrate provides a concise solution. A variety of interfacial strain effects can be achieved by simply controlling the thickness of VO<sub>2</sub> film or using different substrates during the experiment, avoiding film damage and device fatigue effects caused by external mechanical action. However, the device is not adjustable after molding, so the related devices designed by using interface strain require different experimental schemes to find the ideal strain effect, which limits its development in the field of continuous tuning devices. Moreover, the characteristics of external force deformation, which hinders its development in flexible electronic devices.

*External Mechanical Deformation*: In addition to using interfacial strain to change the phase transition characteristics of VO<sub>2</sub>, the use of external mechanical effects to deform VO<sub>2</sub> film is also a promising VO<sub>2</sub> strain engineering adjustment scheme. External mechanical deformation make the VO<sub>2</sub> film undergo macroscopic visible bending, through this external force bending to stretch or compress the VO<sub>2</sub> lattice structure, and then achieve the purpose of changing the VO<sub>2</sub> phase transition temperature and physical properties before and after phase transition.

For example, Tian et al.<sup>[99]</sup> of Fudan University designed the structure as shown in the Figure 11b, rolling VO<sub>2</sub> nanomembranes upwards into VO<sub>2</sub> microtubes with a controllable diameter range, generating significant compressive strain and accommodating them, thereby reducing the phase transition temperature and phase transition threshold voltage of VO<sub>2</sub> materials, which provides ideas for the study of VO<sub>2</sub> actuators device.



**Figure 11.** a) The growth schematic for  $VO_2/Al_2O_3$  interface. Reproduced with permission.<sup>[98]</sup> Copyright 2019, Institute of Physics. b) Schematic of the fabrication of the Cr/VO<sub>2</sub> bimorph structure by selective etching of the SiO<sub>2</sub> sacrificial layer. Reproduced with permission.<sup>[99]</sup> Copyright 2018, American Chemical Society. c) External mechanical effect is applied to  $VO_2$  film on fluorophlogopite (001). Reproduced with permission.<sup>[96]</sup> Copyright 2022, WILEY-VCH.

In 2022, Wang et al.<sup>[96]</sup> studied the external strain engineering dynamic phase transition modulation of quasi-van der Waals VO<sub>2</sub> film on fluorophlogopite, as shown in the Figure 11c, in which the quasi-van der Waals epitaxy on thin fluorophlogopite can minimize the clamping effect of the substrate, obtain a film without interfacial strain, and facilitate mechanical deformation. Through the experiments on the electrical response of VO<sub>2</sub> film at room temperature, it is found that the resistance of the film gradually increases with the increase of external tensile strain and decreases with the increase of compressive strain, and finally it is concluded that the external stress changes the lattice of epitaxial VO<sub>2</sub>, and changes its electronic structure and band gap.

The **Table 3** summarizes the relevant works of external mechanical deformation in recent years. The lattice distortion is introduced by external mechanical change to realize the phase transition modulation of VO<sub>2</sub> from the macro to the microscopic perspective, which provides a macroscopic control scheme for VO<sub>2</sub> materials. Obviously, this adjustment method has a strong continuous tuning ability, which has certain application prospects in filtering devices. In addition, the bendable adjustment method also creates the possibility of the application of flexible devices of VO<sub>2</sub> materials. However, the introduction of external mechanical deformation can easily cause VO<sub>2</sub> structural damage, and the mechanical fatigue of the substrate is also a problem that cannot be ignored.

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## 4.4.2. Strain Engineering Modulation Mechanisms

The strain engineering modulation mechanisms is closely related to the modulation methods used. The principle involved in adjusting the VO<sub>2</sub> phase transition using interfacial strain is lattice mismatch, as shown in the Figure 11. The mismatch between the lattice structures changes the parameters of the VO<sub>2</sub> crystal structure at the interface, which is manifested microscopically as a change in the length of the crystal axis, and therefore VO<sub>2</sub>

Table 3. Study of the methods of strain engineering and the effect of modulation of the VO<sub>2</sub> phase transition temperature.

Date	Strain method	Starin Parameter	Substrate	Film thickness	Тс	Ref.
2018	Interfacial strain	N/A	TiO <sub>2</sub> (001)	20 nm	320.15 K	[97]
2018	External mechanical deformation	-0.5%	SiO <sub>2</sub>	28 nm	329 K	[99]
2019	Interfacial strain	N/A	c– Al <sub>2</sub> O <sub>3</sub>	8 – 62 nm	N/A	[ <mark>98</mark> ]
2020	Interfacial strain	N/A	TiO <sub>2</sub> (001)	8/16/32 nm	N/A	[100]
2020	Interfacial strain	N/A	TiO <sub>2</sub> (001)	60 nm	≈315 K	[101]
2021	External mechanical deformation	-0.4% - 0.4%	Muscovite	100 nm	7.1 K/	[102]
					1% strain	
2021	Interfacial strain	N/A	Al <sub>2</sub> O <sub>3</sub> (001)	≈27 nm	335.15 К —	[18d]
				≈69 nm	329.15 K	
2022	External mechanical deformation	-0.125% - 0.1%	Fluorophlogopite	93.3 nm	335.75 К —	[96]
					347.83 K	

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phase transition properties are changed. Some researchers have reported the interfacial strain effect caused by lattice distortion from different angles.

In 2019, Sang et al.<sup>[18d]</sup> found that on the c-Al<sub>2</sub>O<sub>3</sub> substrate, the VO<sub>2</sub> film thickness decreases, the compressive strain along the b-axis of the VO<sub>2</sub> lattice structure increases, and the farther away from the sapphire substrate, the greater the interfacial relaxation and the greater the lattice mismatch.

In 2020, The D'Elia's team<sup>[100]</sup> reported the strain-induced orbital dynamics of metal insulator transition in VO<sub>2</sub>/TiO<sub>2</sub>(001) films, and they point out that in the early stages of epitaxial growth, tensile strain occurs in VO<sub>2</sub> films to match the substrate lattice, resulting in an increase in both  $a_R$  and  $b_R$  resulting in elastic compression of cr. With the increase of VO<sub>2</sub> film thickness, the distortion caused by the substrate lattice gradually weakens, and the lattice constants relaxes to the bulk VO<sub>2</sub> values. A. D'Elia also explained the effects of film thickness and substrate on VO<sub>2</sub> lattice changes, which has a guiding value on the study of VO<sub>2</sub> interfacial strain.

For external mechanical deformation, the corresponding VO<sub>2</sub> lattice distortion can also be achieved through the external macrostrain modulation of external mechanical deformation, but unlike lattice mismatch, the macrostrain modulation is reflected in the macroscopic, and the effect of controlling lattice distortion is more obvious and the control accuracy is higher. The aforementioned Tian et al.<sup>[99]</sup> and Wang et al.<sup>[96]</sup> achieved lattice macrostrain through a series of external mechanical deformations, which in turn changed the phase transition characteristics of VO<sub>2</sub>. In addition, in strain engineering research, the measurement criteria of lattice distortion involved in large strain and lattice mismatch is often different.

For the VO<sub>2</sub> phase transition induced by strain engineering, in addition to the basic strain mechanism explanation at the lattice distortion level, the explanation of electron orbitals and energy bands based on crystal field theory has also tended to be unified in recent years.<sup>[18d,96,97,101,102]</sup> Among them, Sang et al.<sup>[18d]</sup> gave a more detailed explanation:

When the lattice strain ( $\epsilon_{\rm bM}$ ) decreases, the length of  $a_{\rm R}$  and tip V-O bonds increases,  $c_{\rm R}$ ,  $c_{\rm R}/a_{\rm R}$  and  $\epsilon_{\rm aR} = \epsilon_{\rm bR}$  decrease, while the equatorial V—O bond length almost remains at the same. According to crystal-field theory, as the apical V—O bond length increases, the p-d overlap (O 2p and V 3d orbitals) decrease, which will decrease the energy level of  $\pi^*$  orbitals relative to those of  $d_{//}$  orbitals. Thereafter, this relative energy transfer will result in an increase in the occupancy of  $\pi^*$  orbitals, while the occupancy of  $d_{//}$  orbitals will reduce. The energy of the  $\pi^*$  valence electronic states is lowered, thus a portion of itinerant electrons are transferred from  $d_{//}$  orbitals to the  $\pi^*$  orbitals, reducing electronelectron interaction and stabilizing the metallic state, thereby triggering a lower T<sub>C</sub>.

In addition, the change in the occupancy rate of  $d_{//}$  and  $\pi^*$  orbits can also be expressed as the movement of the corresponding energy band, taking the above process as an example, the reduction of the  $c_R$  axis length will lead to energy  $d_{//}$  band moves upward, and the energy  $\pi^*$  band moves downward, which changes the relative position of the Fermi energy level and varies the band gap size, which in turn leads to the occurrence of a low phase transition temperature of VO<sub>2</sub> material. In short, the purpose of strain engineering is to use

strain to change the band gap or electronic properties of the materials, and then change the phase transition characteristics of  $VO_2$ .

#### 4.5. Magnetic Field Modulation

After studying the classical thermal, electrical, optical, and strain modulation, some researchers began to turn their attention to magnetic field, and through research findings, magnetic fields can also modulate VO<sub>2</sub> phase transition. In 2017, Singh et al.<sup>[6a]</sup> of the Indian Institute of Technology Mand first studied the effects of magnetic field on VO<sub>2</sub> resistivity across MIT, as shown in the **Figure 12**a, when a 1/3/5T magnetic field is applied, a decrease in resistance is observed but no change in T<sub>C</sub>, and the temperature coefficient shifts from negative to positive when a magnetic field is applied, which is finally believed to be related to delocalization of electrons.

In 2020, Matsuda et al.<sup>[6b]</sup> of the University of Tokyo successfully induced the metallization of VO<sub>2</sub> films doped with W under a 500T ultra-high magnetic field, and found that the transmitted light intensity was significantly reduced in the ultra-high magnetic field region, which was believed to be due to the spin Zeeman effect on the d electrons of V ions dissociating the dimers in the insulating phase, resulting in delocalization of electrons (as shown in the Figure 12b). Magnetic field-induced metallization suggests that dimerization is a more important driver of MI transition in VO<sub>2</sub> than electron correlation.

In 2022, Zhang et al.<sup>[104]</sup> demonstrated a VO<sub>2</sub> based micropillar array coated with chromium or Au/SiO<sub>2</sub> layer, as shown in the Figure 12c–f, the input voltage to the solenoid generates an magnetic field H, H $\perp$  component causes in-plane eddy current, and the Joule heating generated by the flowing eddy current rapidly raises the temperature of the VO<sub>2</sub> layer above T<sub>C</sub>, resulting in MIT in the VO<sub>2</sub> layer, realizing a new pathway of VO<sub>2</sub> phase modulation. In addition, this remote control of the electromagnetic field enables the directional transport of SiO<sub>2</sub> particles in liquid media by the  $\alpha$  VPA operating surface. This study proposes a manufacturing method for functional electromagnetic field remote control device based on VO<sub>2</sub>, which provides a new idea for the design of electromagnetic field response structure, which is of great significance for the research and application of magnetron VO<sub>2</sub> phase transition.

Finally, in some reports, some characters choose magnetic interface materials, based on the principle of magnetoelastic coupling, and design VO<sub>2</sub> composite structures that can be controlled by magnetic field. For example, Wei et al.<sup>[29a]</sup> designed a PCAMR device, as shown in the Figure 10c, using the heterostructure of the combination of strongly correlated electronic material VO<sub>2</sub> and spintronic material NiFe, under different optical power irradiation, the magnetoresistive characteristics of the device change, based on this, they used the co-control of light and magnetic field to control the six different resistance states realized in the PCAMR device to design a circuit link that meets the logic application. Although the influence of magnetic field on VO<sub>2</sub> phase transition is not involved, such research provides a new direction for the control means of VO<sub>2</sub>-based devices, which is of great significance to the development of VO<sub>2</sub> magnetron devices.



 $\Psi_{\rm h} \sim \varphi_{\rm b}$ 



Figure 12. a) Metal to insulator transition as depicted by change in resistance during heating at different applied magnetic fields. Reproduced with permission.<sup>[6a]</sup> Copyright 2017, Elsevier B.V. b) The left side shows that the potential barrier  $\Delta$  is lowered because of the Zeeman energy. The middle part schematically shows the collapse of the V-V dimers. The right part shows that applying a magnetic field induces the dissociation of the dimer owing to the destabilization of formation of the bonding state  $\Psi$  of the molecular orbital, where  $\varphi$ a and  $\varphi$ b are the wave functions of the independent vanadium ions. Reproduced with permission.<sup>[6b]</sup> Copyright 2020, Springer Nature. c) A glass beaker containing VPA specimens ( $\alpha$  or  $\alpha$ +) and media (air or water) is put inside a solenoid. By inputting UC, a high-frequency AC current is generated with an AC inverter, and H with 50 kHz is created along central axis of the solenoid; d) Two components of primary magnetic field H, H// and H⊥; e) The resulting two eddy current loops (yellow loop), one is out of plane and the other is in-plane; f) A detailed description of electromagnetic field responsive VPA under HL. High-frequency primary magnetic field HL (red loop) generates in-plane eddy current (yellow loop) across the metal layers of  $\alpha$  and  $\alpha$ + and this eddy current then induces a secondary magnetic field (green loop) opposite to the primary HL. Reproduced with permission.<sup>[103]</sup> Copyright 2022, WILEY-VCH.

In summary, magnetic field control provides a new way to change the electron state through Zeeman splitting, achieving a significant quantum-mechanical electron correlation at low temperatures.<sup>[6b]</sup> In addition, electromagnetic fields can easily and harmlessly penetrate most biological materials and liquid media without absorbing energy, which has important application value in the medical field. Moreover, compared with the light field modulation in the environment, the magnetic field modulation is more stable.<sup>[103]</sup> At present, there are few reports on magnetic field modulation of VO<sub>2</sub> phase transition, and in-depth research is still needed, and magnetron is expected to become an excellent control method for VO<sub>2</sub> devices in the future, accelerating the development of VO<sub>2</sub> in spintronic devices.

## 5. Elemental Doping Optimizes The Performance of VO<sub>2</sub>-Based Devices

Although VO<sub>2</sub> is a strongly correlated material with great potential for application, the development of VO<sub>2</sub> film in optical and electrical devices has been restricted by several drawbacks in performance, including high phase transition temperature (T<sub>c</sub>), low luminous transmittance (T<sub>lum</sub>), insufficient solar energy modulation ability ( $\Delta T_{sol}$ ) and unpopular color.<sup>[33]</sup> However, the researchers found that other elements can be introduced into the VO<sub>2</sub> system by doping, and the composite material is modified relative to the original pure VO2 material through physical or chemical processes, retaining the original phase transition characteristics, and the phase transition temperature and physical

properties change before and after the phase transition. The following will mainly discuss the methods and modification principle of elemental doping in VO<sub>2</sub> and the modified results reported in recent years.

## 5.1. Elemental Doping Methods

Efficient doping methods help to improve the performance of doped materials or films, and a variety of physical or chemical  $VO_2$  doping methods have been reported, such as high-temperature melting, hydrothermal, sol-gel, chemical vapor deposition, magnetron sputtering, electron-beam evaporation, pulsed laser deposition, ion implantation, atomic layer deposition, etc. The following briefly introduces the content of each doping method and analyzes its advantages and disadvantages.

Most of the early doping method was high-temperature melting, in which oxides containing doped elements and VO<sub>2</sub> were subjected to high-temperature solid phase reaction under vacuum or inert gas to generate products similar to V<sub>1-x</sub>M<sub>x</sub>O<sub>2</sub> (M is doped ions) to complete ion doping.<sup>[105]</sup> This method is simple and more convenient for preparing large-bulk doped and multi-element co-doped materials with flexible proportions. In addition, because the doped oxides are not completely diffused into the VO<sub>2</sub> lattice, the grain boundaries are strengthened and the mechanical strength of the synthetic materials is improved.<sup>[106]</sup> However, the high energy consumption of the melting process increases the cost, and the process takes several days to complete, which reduces the efficiency and convenience of production.<sup>[106,107]</sup>

Compared with high-temperature melting, hydrothermal and sol-gel methods add dopants to the precursor, which can synthesize impurity ion-doped VO<sub>2</sub> at a lower temperature with low cost.<sup>[108]</sup> In addition, the hydrothermal method has stable operation and high crystallinity of the product, which is suitable for large-scale production of doped materials. This method may generate metastable monoclinic polymorph  $VO_2(B)$ or oxygen-deficient VO2, which can be converted to M1 phase after annealing.<sup>[109]</sup> However, post-annealing tends to lead to nanoparticle aggregation, and one-step hydrothermal method can improve the dispersion of the product.<sup>[110]</sup> For example, Wanxia Huang et al.<sup>[110b]</sup> used tartaric acid as a reductant to produce high-purity VO<sub>2</sub>(A) under hydrothermal conditions, due to  $VO_2(A)$  had a better  $VO_2(M)$  conversion rate than  $VO_2(B)$ ,<sup>[111]</sup> the final W-doped VO<sub>2</sub> yield increased. Unlike the hydrothermal method, the sol-gel method, in which the precursor is a gel that is dried to obtain the product, is a more complex process. The material prepared by this method has high purity and good uniformity, and due to the good film-forming property of the gel, the precursor can be used to directly make the film, and the elementdoped VO<sub>2</sub> film can be made by drying.<sup>[112]</sup> In addition, the solgel method does not require vacuum to ensure the quality of film formation, and the reaction process is easier to control, which has become a common method for the preparation of doped-VO<sub>2</sub> films.<sup>[113]</sup>

As a traditional doping method, ion implantation implants high-energy doped ion into the film/material, and the selection of doping material is not limited by diffusion kinetics and solid solubility in the film, which has great application potential in  $VO_2$  membrane elemental doping. In 1977, German scientist Ufert<sup>[114]</sup> prepared highly doped  $VO_2$  films at very low substrate temperatures, overcoming the shortcoming of high temperature for doping. Ion implantation has therefore become an important method of elemental doping at room temperature. However, the impinging ions deposit energy along the path of the host material through nuclear and electron collisions, resulting in damage such as defect generation, amorphization, recrystallization, randomization, and surface morphology changes, which affect the thermochromic properties of the film/material.<sup>[115]</sup>

The development of thin film deposition technology provides a new way for the doping of elements in VO<sub>2</sub> films. Chemical vapor deposition uses the chemical reaction of gas precursors to deposit solid films on the surface of the substrate, among which atmospheric pressure chemical vapor deposition (APCVD) is more widely used in doped-VO<sub>2</sub> films.<sup>[116]</sup> Compared with other film deposition techniques, APCVD has the advantages of conformal coverage, high growth rate and no low pressure requirement. However, compared with the solution preparation, APCVD has strong selectivity for precursors, and some precursors are easy to be blocked in the mixing chamber and reactor inlet during equipment operation, reducing the doping efficiency. Since the precursor before deposition is the gas phase, the toxicity and contamination of the gas and the residue of impurities are also issues to consider.<sup>[116a]</sup>

In contrast, physical vapor deposition (PVD) through physical processes to make membranes has lower impacts on the environment. There are many types of PVD technologies, such as magnetron sputtering, in which high-energy particles are used to hit the target material, so that solid atoms are ejected from the surface and deposited onto the surface of the substrate to form the film. However, since the sputtering target is metal, doped-VO<sub>2</sub> films cannot be prepared directly, so reactive magnetron sputtering is considered for the synthesis of V<sub>1-x</sub>M<sub>x</sub>O<sub>2</sub> films. This technology can improve film density, etching rate, adhesion, control smooth surface morphology and control crystal size, and improve the performance of doped films.<sup>[117]</sup> However, the sputtering rate of the magnetron target varies with its lifetime, so in order to obtain a stoichiometric doped film, precise control of the partial pressure of oxygen is required.<sup>[118]</sup> Unlike magnetron sputtering, electron beam evaporation uses an electron beam to heat the evaporated material in a vacuum state, and can directly form a deposited film on the substrate without the participation of reactive gases. In 2017, Shao-En Chen et al.<sup>[119]</sup> successfully prepared W-doped VO<sub>2</sub> films for the first time using a single target source (treated WO<sub>3</sub>/VO<sub>2</sub> mixed powder) and post-annealing. In addition, the deposition rate of this process is high and the appearance of other oxidation states of V is largely avoided.<sup>[120]</sup> However, the high cost of the equipment hindered its further development. Similar to electron beam evaporation, pulsed laser deposition (PLD) uses a high-power pulsed laser beam to evaporate the target material and deposit it on the substrate, and the laser energy used for evaporation is high, which can be used to sputter various refractory materials. For example, Chen et al.<sup>[121]</sup> successfully deposited Al3+-doped VO2 films by using PLD to ablate V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> composite targets. In addition, for some targets, reaction gas can also be introduced in the PLD process for reactive pulsed laser deposition (RPLD). For example, Wang et al.<sup>[32]</sup> used Hf-doped V targets to deposit Hf-doped VO<sub>2</sub> films in

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ambient O<sub>2</sub> gas. Hajlaoui et al.<sup>[122]</sup> deposited boron-doped VO<sub>2</sub> films in oxygen flow with chimeric vanadium/boron targets. It can be seen that the target material of PLD is more flexible in selection and faster deposition. However, the substrate temperature has influence on the deposition of thin films, and the equipment is expensive, which is not suitable for low-cost production.

Finally, Atomic layer deposition (ALD) is also commonly used in the elemental doping of VO2 films. Different from the CVD that continuously introduces the gas-phase precursor, ALD is a advanced film deposition technology by alternately pulsing the gas-phase precursors into the reaction chamber, and based on the self-limiting growth mechanism, the gas-solid phase chemical adsorption reaction occurs on the surface of the substrate for atomic-level film growth. The nanolaminates at the nanometer thickness scale obtained by deposition are initially in a nonequilibrium state with large interface energy, which is thermodynamically conducive to interlayer diffusion. By annealing, ALD can achieve doped films with continuously adjustable solubility, good homogeneity and high conformality.<sup>[123]</sup> In 2018, Lv et al.<sup>[123a]</sup> first used ALD to realize VO2-doped films, and they used V(NMe2)4 and Mo(CO)<sub>6</sub> as precursors of V and Mo, deposited alternating VO<sub>2</sub>/MoO<sub>3</sub> nanolayer films through the ALD process, and after annealing, the alternating layers were penetrated and mixed, and they successfully got the  $V_{1,x}M_xO_2$  films with excellent thermochromic properties. Later, Shin et al.[123d] used VTOP and TMA as precursors of V and Al, and obtained Al-doped VO<sub>x</sub> films by ALD process and annealing. It can be seen that ALD can easily mix precursors without melting ingots. However, due to the ALD mechanism, the deposition rate is slow. In short, different doping methods have their own advantages and disadvantages, and the optimization of elemental doping technology for VO<sub>2</sub> films still needs to be explored.

#### 5.2. Modulation of The Phase Transition Temperature T<sub>c</sub>

 $VO_2$  has been found to have an insulation-metal phase transition around T = 340K, but in different application environments, the phase transition temperature (T<sub>C</sub>) required for  $VO_2$  in  $VO_2$ -based devices is different, so the modulation of phase change temperature has become the focus of research on  $VO_2$  materials and their devices.

The earliest, W. Rüdorff et al.<sup>[105a]</sup> tested the molar magnetic susceptibility temperature dependence curves of mixed crystals with different VO<sub>2</sub> contents and found that there was a difference in the transition temperature T<sub>C</sub>, indicating that elemental doping had the potential to change T<sub>C</sub> of VO<sub>2</sub>. In 1969, J. B. Mac-Chesney and H. J. Guggenheim<sup>[124]</sup> studied the characteristics of VO2 single crystals containing different impurity ions and found that the transition temperature T<sub>C</sub> changed significantly under high levels of doping, and the direction of change in  $T_{\rm C}$  was related to the relative size of the impurity ions, and T<sub>C</sub> was not affected by carrier concentration. In the same year, M. Israelsson of Stockholm University and others studied the relationship between the  $V_x W_{1,x} O_2$  crystal structure and x, and found that the transition temperature T<sub>c</sub> decreased linearly with the increase of x.<sup>[125]</sup> In 1971, J. B. Goodenough<sup>[18b]</sup> summarized the mathematical relationship between the doping ratio of various impurity ions and Tc variation by studying the influence of elemental doping on

the structural changes of VO<sub>2</sub> three-phase crystals, further promoting the development of elemental doping in VO<sub>2</sub>. After that, Western scientists did a lot of work on the elemental doping in the VO<sub>2</sub> system, gradually improved the doping system of VO<sub>2</sub>, and revealed the doping mechanisms.

The mechanism of elemental doping changing the phase transition temperature  $(T_c)$  of VO<sub>2</sub> has been developed for many years, and the current dominant explanations mainly combine microscopic lattice and carrier changes with energy level theory: i) Ions are introduced into the VO<sub>2</sub> lattice, and lattice distortion is caused by the mismatch of ion diameter length (Figure 13a), which affects electron correlation and orbital occupancy, and changes the original band distribution, thereby affecting T<sub>c</sub>; (ii) Injecting carriers (electrons or holes) into the VO<sub>2</sub> system through the valence electron difference between elements, generating  $V^{3+}$  ions (Figure 13e), breaking  $V^{4+}$ - $V^{4+}$  dimmer, or the addition of free electrons can not only enhance coulomb shielding and inhibit the splitting of  $d_{11}$  orbital, but also raise the Fermi level (Figure 13f), thereby stabilizing the metallic phase; (iii) Cooperative interaction. In recent years, with the deepening of the study of elemental doping, in the process of elemental doping to change T<sub>C</sub>, especially multi-element co-doping, scientists have found that lattice distortion and carrier injection work together to change the magnitude of the phase transition temperature  $(T_{\rm C}).^{[34a,126]}$ 

In 2019, Chen et al.<sup>[18a]</sup> used first-principles calculations to study the mechanism of rare-earth (RE) elemental doping affecting  $T_{\rm C}$ . Experiments show that due to the long ion radius of RE, its incorporation causes local distortion of the original VO<sub>2</sub> system, and based on the research of Xie et al. ,<sup>[127]</sup> the researchers believe that this distortion affects the band gap and thus drives the occurrence of VO<sub>2</sub> MIT. In addition, based on the difference in electronegativity between rare earth ions and V atoms, Chen et al.<sup>[18a]</sup> finally suggested that the reduction of  $T_{\rm C}$  may be related to the counteraction of electron/hole carriers and the competition between the strain and the hole carriers.

In 2021, Wang et al.<sup>[32]</sup> tried to incorporate Hf and Mg ions in the VO<sub>2</sub> system, and found the presence of low-valent V ions and architectural changes in the VO<sub>2</sub> system through the XRD spectrum and XPS spectrum after elemental doping, indicating that Hf-W co-doping caused electron injection and lattice distortion, the former reducing the number of V<sup>4+</sup>—V<sup>4+</sup> bonds in stable low-temperature monoclinic states, and the latter weakening V-V dimerization and enhancing lattice strain, both contributing to the reduction of T<sub>C</sub>.

In 2022, Yang et al.<sup>[34a]</sup> studied the cooperative effect of La-Mo co-doping in the VO<sub>2</sub> system, first of all, Mo dopants can achieve the same electron injection ability as W, electron doping leads to the formation of V<sup>3+</sup>, breaks the dimerization of V<sup>4+</sup>-V<sup>4+</sup> in the insulating state, stabilizes the metal state, and reduces T<sub>C</sub>; Second, the incorporation of large radius La ions will cause large compressive stress on the c axis of the VO<sub>2</sub> tetragonal structure, which also contributes to the reduction of T<sub>C</sub> (Figure 13g).

Studying the mechanisms of VO<sub>2</sub> phase transition temperature change caused by elemental doping is conducive to exploring the optimal modification strategies of VO<sub>2</sub> material and promoting the practical application of VO<sub>2</sub> in the future. This is macroscopically manifested in the exploration of doping





**Figure 13.** The calculated super-cell structures of a) pure M1-VO<sub>2</sub> ( $V_{32}O_{64}$ ), b) Hf-doped M1-VO<sub>2</sub> (Hf<sub>4</sub> $V_{28}O_{64}$ ), and c) Hf–W co-doped M1-VO<sub>2</sub> (Hf<sub>4</sub> $W_{1}V_{27}O_{64}$ ). Reproduced with permission.<sup>[32]</sup> Copyright 2021, American Institute of Physics. d) Band structure of VO<sub>2</sub> (M) for different Zr doping concentrations: no doping; 2.08% doping; 4.17% doping (from left to right). Reproduced with permission.<sup>[128]</sup> Copyright 2022, American Chemical Society. e) XPS survey spectrum of the effect of high valence ion doping on formation of V<sup>3+</sup> ions: 1 at.%, 1.5 at.% and 2 at.% W doped VO<sub>2</sub> annealed at 470 °C. Reproduced with permission.<sup>[126c]</sup> Copyright 2017, Springer Nature. f) electronic phase transition toward a metallic phase via hydrogen donation of electron carriers that fill the energy band gap. Reproduced with permission.<sup>[129]</sup> Copyright 2022, American Chemical Society. g) Schematic of the orbital change of the La-Mo co-doped VO<sub>2</sub> films. Reproduced with permission.<sup>[34]</sup> Copyright 2022, Elsevier B.V.

elemental types, doping concentrations and co-doping ratios, and **Table 4** lists the research progress of VO<sub>2</sub> elemental doping modification (T<sub>C</sub>), from which it can be seen that elemental types have the greatest impact on VO<sub>2</sub> modification. Different kinds of elements cause different modification effects, which are related to the atomic structure and charge properties of the elements themselves. For example, among many dopants, W is the most effective element to reduce T<sub>C</sub> of VO<sub>2</sub>.<sup>[33,130]</sup> In previous works, the lowest phase transition temperature T<sub>C</sub> achievable through W doping was 160K.<sup>[131]</sup> In addition, in aspect of raising phase transition temperature of the material to 137° with Fe doping. Through years of research, elemental doping has achieved a wide range of adjustment of the phase transition temperature

of new materials, which is meaningful in the application of  $VO_2$ -based optical and electrical devices, especially in the field of smart windows, which has great application potential.

## 5.3. Improvement of Optical Properties

To study the influence of doping on the phase transition of VO<sub>2</sub>, in addition to the phase change temperature, the optical performance modulation of VO<sub>2</sub> is also the focus of studying. The indicators to measure the optical performance of doped thin films are mainly visible light transmittance (T<sub>lum</sub>) at room temperature and solar-modulation efficiency ( $\Delta T_{sol}$ ). The calculation of T<sub>lum</sub> and  $\Delta T_{sol}$  is generally based on the transmission spectrum in a

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**Table 4.** Effect of element type and doping concentration on phase transition temperature ( $T_C$ ).

Date	Doped elements	Doping ratios <sup>a)</sup>	Тс	Reference
2008	Al	10 at.%	40 °C	[121]
2010	Мо	-	−3 °C/at.%	[133]
2011	W	-	-(48–56) K/at.%	[134]
2015	Ti	20 at.%	≈360 K	[135]
2016	Li	-	-43 K/at.% (Calc.)	[136]
2017	Ge	5.9 at.%	93.6 °C	[137]
2018	Fe-Mg	9.2%-7%	36.7 °C	[33]
2019	Tb/La	3.1 at.%	206 K/225 K	[18a]
2019	Nb	6 mol %	25 °C	[138]
2020	Sn-W	1.9 at.%–1.6 at.%	26 °C	[139]
2020	В	-	31.5 °C/at.%	[122]
2021	Fe	12.6 mol %	134 °C	[132]
2021	Та	4 at.%	24.8 °C	[43]
2022	Ar	N/A	31 °C	[140]
2022	La-Mo	1 at.%–1.5 at.%	38 °C	[34a]

<sup>a)</sup> The doping ratio and its calculation standard are article-specific and are not modified by conversion.

certain wavelength range, and the calculation formula is as follows:

$$T_{lum/sol} = \frac{\int \varphi_{lum/sol}(\lambda) T(\lambda) d\lambda}{\int \varphi_{lum/sol}(\lambda) d\lambda}$$
(4)

$$\Delta T_{sol} = T_{sol,LT} - T_{sol,HT}$$
(5)

where T( $\lambda$ ) is transmittance at a wavelength of  $\lambda$ ,  $\varphi_{lum}(\lambda)$  is the standard luminous efficiency function for the photopic vision, and  $\varphi_{sol}(\lambda)$  is the solar irradiance spectrum for air mass 1.5 corresponding to the sun standing 37° above the horizon.<sup>[31,34a,141]</sup>

**Table 5** summarizes the high  $T_{lum}$  and  $\Delta T_{sol}$  achieved in recent years with different elemental doping in specific wavelength ranges. As can be seen from the table, in the visible range of 380 – 780 nm, more than 50% of  $T_{lum}$  and more than 12%  $\Delta T_{sol}$  can al-

Table 5. Effect of element doping on optical properties of thin films.

Date	Doped elements	Tlum_max (380–780 nm)	Wavelength range (∆Tsol)	∆Tsol_max	Reference
2018	Fe-Mg	42.1%	280—2500 nm	12.8%	[34a]
2019	W@PVP	68.3%	250—2500 nm	20.4%	[130a]
2020	Sn-W	64.4%	280—2500 nm	15.4%	[143]
2021	Hf-W	41.1%	780—2500 nm	13.1%	[32]
2021	W@ PNIPAm	92.48%	280—2500 nm	77.20%	[144]
2022	Co	<b>79</b> %	280—4000 nm	12%	[ <mark>3</mark> 1]
2022	ZrO2	51.1%	300—2500 nm	12.6%	[145]
2022	La-Mo	32%	300—3000 nm	> 10%	[34a]
2023	Fo-Mo	59.7%	300—2300 nm	13.7%	[126a]

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ready be achieved. It is noteworthy that VO<sub>2</sub> polymer films doped with low concentrations of elements can often achieve extremely high optical modulation, but this performance stems from the contribution of the polymer itself, not doping, so it will not be discussed in this chapter. In addition, the performance of doped films and the types of doped elements are also inseparable, some elements improve the optical properties of the film more obviously (e.g., Mg, Sn), while some elements are not (e.g., W, Mo). In general, the same element has competition in the ability to adjust  $T_C$  and optimize optical performance, and co-doping can solve this problem, some elements are responsible for reducing  $T_C$ , and some elements are responsible for improving optical performance, which has achieved ideal results in experiments.

For example, in 2020, Zhao et al.<sup>[139]</sup> proposed a method for Sn–W co-doping, adding Sn to W-doped VO<sub>2</sub>, aiming to reduce T<sub>C</sub> by W and widen the optical bandgap by using Sn, improve the transmittance of materials, and realize an efficient smart film. Finally, the experiment found that the film doped with Sn-W was  $\approx$ 1.8 times higher than that when W-doped, but the W doping decreased T<sub>C</sub> did not change significantly, suggesting that codoping offers a new strategy for improving the optical performance of thin films. In 2022, Yang et al.<sup>[34a]</sup> also took advantage of the synergistic effects of La-M co-doping to reduce T<sub>C</sub> by using Mo's large ion radius and high chemical valence. On this basis, La is used to increase the optical band gap of the material and improve the visible light transmittance.

The transmittance of a material is closely related to its band gap, and the wider the band gap, the easier it is for photons with low energy to transmit, so the change in optical properties of the thin film caused by doping can be well explained from this angle. Based on the transmission spectrum study of  $(\alpha hv)^n$ -hv curve relationship, the change of band gap can be obtained, and the relationship between the two is as follows:

$$(\alpha h\nu)^n = A(h\nu - E_g) \tag{6}$$

where  $\alpha$  is transmittance is the absorption factor obtained from the transmittance spectra, h is the Planck constant, v is the optical frequency, hv is the photon energy, A is the constant,  $E_{\sigma}$  is the energy gap of the material. The n in the equation (6) is determined by the properties of the material, n takes 2 corresponds to the direct energy gap of  $VO_2$ , and in some reports, let n =2, calculate the  $E_g$  size of the doped material from the  $(\alpha hv)^2$ -hv curve relationship.<sup>[31,32,34a,142]</sup> For example, Geng et al.<sup>[31]</sup> pointed out that the optical response behavior caused by doping is related to the inherent band gap of the material, and through the above calculations, the optical band gap of the doped material increases significantly, so the transmittance of the doped material increases. In addition, Ji et al.<sup>[33]</sup> let n = 1/2 by linearly fitting the plotted  $(\alpha hv)^{1/2}$ -hv curve, the doped material is calculated to have an optical band gap of up to 1.89 eV, corresponding to the highest T<sub>lum</sub>.

When describing the reasons for the variation in the optical response of doped films, the microtopography of the film is often also taken into account, as shown in **Figure 14**. Xu et al.<sup>[38]</sup> prepared Ta-doped VO<sub>2</sub> film and found that with the incorporation of Ta<sup>5+</sup> ions, the porosity of the film surface increased significantly (Figure 14e–h), this increases the transmittance (T<sub>lum</sub>) of the film at low temperature. Different from the external regulatory factors





Figure 14. Doped film morphology. a) undoped; b) 0.74 at% Sn-doped; c) 1.73 at% Sn-doped; d) 1.86 at% Sn-doped. Reproduced with permission.<sup>[143]</sup> Copyright 2020, Elsevier B.V. e) 0.22% Ta-doped; f) 0.34% Ta-doped; g) 0.71% Ta-doped; h) 2.51% Ta-doped. Reproduced with permission.<sup>[38]</sup> Copyright 2021, Elsevier B.V.

of heat, light, electric and strain mentioned above, element doping should essentially be regarded as an internal structure "modification" that has significant modifying effects on VO<sub>2</sub>, which has development potential in the field of optical devices in the future.

## 6. Progress in VO<sub>2</sub> Application

VO<sub>2</sub> is widely used in optical and electrical devices because of its special phase change properties, especially in recent years, the improvement of device preparation level and the advancement of characterization methods, various high-performance VO<sub>2</sub>-based optical/electrical devices have been reported frequently, such as terahertz modulators, smart windows, sensors, etc. The following mainly introduces the application progress of VO<sub>2</sub> devices from the above specific practical application perspectives.

## 6.1. Terahertz Modulators

Terahertz waves are between infrared and microwave, with all the characteristics of electronics and optics, which can compensate for the shortcomings of microwave communication and optical communication, while terahertz modulators can modulate output according to the required terahertz waves. Vanadium oxide films are semiconductor phase at low temperature and are almost transparent to terahertz waves. At high temperature, VO<sub>2</sub> changes to a metallic phase with increased carrier density, enhanced reflection and absorption of terahertz waves, resulting in low transmittance. Therefore, VO<sub>2</sub> film becomes a popular material for THz wave modulators.<sup>[38,146]</sup>

In 2009, Seo et al.<sup>[147]</sup> first reported that the micro-nano apertures size of the film was controlled by temperature-driven VO<sub>2</sub> substrate refractive index change, and the transmission modulation of terahertz wave (0.1–1.6 THz) was realized, revealing the application potential of VO<sub>2</sub> materials in the field of terahertz wave modulation. Subsequently, VO<sub>2</sub> materials have been extensively studied in the field of terahertz modulator preparation, and a variety of excellent  $\mathrm{VO}_2$  terahertz modulators have been realized.

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From the perspective of control conditions, due to the characteristics of VO<sub>2</sub> multi-condition induced phase transition, VO<sub>2</sub> terahertz modulators have developed different control methods (thermal, electrical, optical). As shown in the **Table 6**, different control methods implement different modulator performance. For example, the modulator response speed of optical and electrical trigger is faster than that of thermal trigger, and it has been reported that the principle of optical pump excitation carrier can be used to control the passage of terahertz waves, and the response speed reaches the order of ps.<sup>[16d]</sup> However, the thermal trigger can achieve room temperature modulation by reducing  $T_C$  by doping. In short, different control conditions have their own advantages, and the specific choice depends on the actual application conditions.

A terahertz modulator is evaluated by its modulation depth (MD), bandwidth, response speed, or trigger threshold. First, The THz field amplitude modulation depth results from a large change in carrier concentration, defined as:

$$Md = \frac{E_I - E_M}{E_I} \tag{7}$$

where  $E_1$  and  $E_M$  are the THz field amplitudes at insulating and metallic states of a VO<sub>2</sub> film, respectively. Increasing the modulation depth is critical to the modulation scale and signal control of the modulator, and there are many ways to achieve it. For example, Zhao et al.<sup>[16d]</sup> used low-light pump energy to excite Si substrates to generate carriers, which reduced terahertz wave transmittance without triggering the VO<sub>2</sub> phase transition and exciting VO<sub>2</sub> large concentrations of carriers. Ma et al.<sup>[146]</sup> found that by increasing the VO<sub>2</sub> film thickness in VO<sub>2</sub>/CNT, it was possible to increase the MD from 26% to 87%, achieving a huge change in modulation depth. In addition, high modulation depth can be achieved by setting the metasurface structure to change the optical transmission of the device.<sup>[16d,148]</sup> In general, high modulation

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#### Table 6. Research progress of terahertz modulator in recent years.

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Date	Sample	Modulation Depth	Bandwidth [THz]	Response time	Triggering threshold	Insert loss	Reference
2018	Nb doped VO <sub>2</sub>	64%	4.8 to 5.4	N/A	Thermal: 31.1 °C	N/A	[149a]
2018	VO <sub>2</sub>	97.6% at	N/A	N/A	Thermal: 95 °C	N/A	[151]
		0.5 THz					
2018	Al/Si <sub>3</sub> N <sub>4</sub> /VO <sub>2</sub> Metasurface	99% at	0.5	N/A	Electrical:	N/A	[152]
		0.45 THz			0.28 A		
2019	VO <sub>2</sub> /Mica	81.2%	N/A	120 ms	Light:	N/A	[149b]
					0.13 mJ cm <sup>-2</sup>		
2019	VO <sub>2</sub> /	94%, Average	0.2 to 2.0	N/A	Thermal: 70 °C	N/A	[153]
	c-sapphire						
2020	Graphene/VO <sub>2</sub>	96%, Average	0.3 to 1.5	N/A	Electrical: -	-4.1	[154]
2020	VO <sub>2</sub> /CNT	91%, Average	0.2 to 2.5	5 ms	Light:	2.2 dB	[146]
					$0.58 \text{ mW mm}^{-2}$		
2021	VO <sub>2</sub> /PVP	65%	$\approx$ 0.32 to 0.5	N/A	Light:	N/A	[155]
					4.3 mW mm <sup>-2</sup>		
2021	$Si_3N_4$ - $VO_2$ - $Si_3N_4$	99% at	N/A	100 ms	Electrical:	N/A	[156]
		0.8 THz			0.3 A		
2022	Si/VO <sub>2</sub> Metasurface	97.2% at	0.4 to 1.8	2 ps	Light:	N/A	[16d]
		0.9 THz			$1600 \ \mu W \ cm^{-2}$		
2022	VO <sub>2</sub>	99.9% at	0.35 to 0.76	1 s	Electrical:	N/A	[150]
		0.55 THz			18 mA		
2022	VO <sub>2</sub> patterns	68%	$\approx$ 0.1 to 0.8	1.9 s	Electrical:	N/A	[157]
					520 mA		
2023	Cu@SiO <sub>2</sub> /	73%, Average	N/A	N/A	Thermal: 70 °C	N/A	[148b]
	VO <sub>2</sub> @SiO <sub>2</sub>						

depth means that a large number of signals can be controlled, increasing the diversity of modulation. As shown in the Table 6, some current studies have achieved modulation depth of more than 99% at specific frequencies and 90% average modulation depth in a certain band.

In addition, low modulation threshold have been the focus of VO<sub>2</sub> terahertz modulators, which is critical to reducing the cost of modulators. There are many ways to achieve a low trigger threshold, such as doping, choosing the right substrate, and so on. However, elemental doping increases carrier concentration and decreases carrier concentration variation, thereby weakening the modulation depth, which greatly affects modulator performance.<sup>[109a,149]</sup> For example, Li et al.<sup>[148b]</sup> found that the vdW bond between the mica substrate and the VO<sub>2</sub> film was used to avoid the clamping effect, reduce the lattice effect of the film and the substrate, and reduce the heat conduction of the film to the substrate because of the weak lattice coupling, and finally reduce the trigger threshold and keep ideal Md.

Due to the hysteresis of VO<sub>2</sub>, electro-optical terahertz modulation has a historical dependence, which affects control and accuracy. For this reason, Ren et al.<sup>[150]</sup> use a computer control program to receive the output signal PR in real time and adjust the input signal Ia for feedback, and automatically adjust the input signal when the output signal deviates from the expected.

Compared with other electromagnetic waves, terahertz wave has high penetration, high resolution, low energy, and outstanding transient performance, and based on this, terahertz technology is expected to be widely used in medical imaging, safety screening and material spectroscopy. The development of various terahertz manipulation devices is the application prerequisite of terahertz technology. At present, THz AMs based on VO<sub>2</sub> can achieve considerable Md, low insertion loss and perfect broadband response, successfully combining terahertz technology with VO<sub>2</sub> materials, with broad market prospects.

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## 6.2. Sensors

The sensor is a detection device that converts the detected information into electrical signals or other required forms of information output according to certain rules to meet the requirements of information transmission, processing, storage, display, recording and control. The following mainly introduces the development of VO<sub>2</sub>-based sensors from different types of sensors.

The thermochromic properties of VO<sub>2</sub> indicate a large temperature coefficient of resistance (TCR) near T<sub>C</sub>, which is attractive in the design of heat measurement.<sup>[49]</sup> The heat that affects the physical properties of VO<sub>2</sub> can be provided by photoirradiation, so VO<sub>2</sub> has become a new candidate material in the field of bolometer. Already in the last century, VO<sub>2</sub>-based bolometer arrays were reported. And Zerov et al.<sup>[158]</sup> studied the operating characteristics of VO<sub>2</sub>-based bolometer in the phase transition temperature range, and found that a large amount of noise caused by phase transition occurred, and the excess noise is dependent on current and frequency.

The hysteresis characteristics of VO<sub>2</sub> are extremely detrimental to the application of bolometers and need to be improved.<sup>[16f]</sup> In recent years, bolometer have been improved, such as Ainabayev et al.<sup>[44b]</sup> to control the SMT parameters of growing ultrathin epitaxial VO<sub>2</sub> samples by changing grain size and oxygen vacancy concentration. Wide TCR (2.1–53.9%) and RT resistivity values (0.0019–1.02  $\Omega$  cm) are provided in a wide  $\Delta$ T (10 – 35 K) range, accompanied by a very low  $\Delta$ H variable between 0.2–2.

Different from the photothermal effect, Kabir et al.<sup>[159]</sup> designed a photophysical sensor with different light responses in the broadband range from ultraviolet to near-infrared to display excellent sensing performance.

In addition to phase change characteristics, vanadium dioxide can also be electrochemically oxidized, can be used as an electrochemically stable material in oxidation and reduction process, and it shows great flexibility in inorganic networks for chemical detection and application in the field of chemical sensors. For example, E.M. Guerra's team used VO<sub>2</sub> thin film to modify the electrode to make the electrode surface have high electrochemical porosity, so that the sensor showed superior sensitivity and a large electrochemical activity region, and achieved 61.5 mV/pH (pH = 5–8)<sup>[160]</sup> and 33.9 mV/pH (pH = 4-10)<sup>[161]</sup> sensitivity in AZI and glucose sensor designs, respectively.

In the chemical sensor there is a type of sensor for detecting gas-gas sensor, some researchers have designed a variety of gas sensors according to the special role of VO<sub>2</sub> and gas molecules (gas molecules are adsorbed or desorbed by the surface of VO<sub>2</sub> film, thereby changing the electron concentration on the surface of VO<sub>2</sub>, and then changing the physical characteristics of film resistance and light absorption). For example, Simo et al. et al.<sup>[162]</sup> demonstrated for the first time that VO<sub>2</sub> has ideal hydrogen sensing capabilities at room temperature. Recently, Joy et al.[163] used DFT and molecular dynamics to study the gas-sensitive characteristics of gold-doped vanadium dioxide, and found that CH<sub>4</sub> adsorbed Au-VO<sub>2</sub> system has the smallest adsorption distances and energies, and through Hhirshfeld charge transfer analysis and CDD and DOS calculations, it is inferred that CH<sub>4</sub> molecules have obvious electron transfer to Au-VO2 system, and it is concluded that  $\text{Au-VO}_2$  has strong sensing characteristics for  $\text{CH}_4$ gas. Huang et al.<sup>[164]</sup> studied the H<sub>2</sub>S sensing mechanism on the

Pd/VO<sub>2</sub> surface and found that the adsorption process of  $H_2S$  gas on the intrinsic VO<sub>2</sub> surface was spontaneous, and the adsorption characteristics of  $H_2S$  were improved by loading the Pd at the optimal position. And they found that VO<sub>2</sub>+Pd+H<sub>2</sub>S film has the strongest response to visible light, which provides theoretical support for the fabrication of optical gas sensors. Rahman et al.<sup>[165]</sup> even successfully set up an NFC detection system based on the charge transfer characteristics between nicotine and VO<sub>2</sub>, as shown in the **Figure 15**.

In recent years, the demand for wearable sensing devices has driven the development of flexible sensing devices. VO<sub>2</sub> is an excellent choice for flexible sensors due to its fast switching speed, diverse trigger conditions, strong non-volatility, excellent scalability and ability to work at room temperature. For example, Li et al.<sup>[166]</sup> chose to deposit VO<sub>2</sub> film on mica substrate, and after bending test, it was found that the phase transition process of VO<sub>2</sub> film induced by ultraviolet light was almost not affected by bending, and showed good bending stability.

On the other hand, in some conditions, some flexible sensors take advantage of their bendable characteristics as strain sensors. For example, Huang et al.<sup>[167]</sup> prepared VO<sub>2</sub> nanowires on a flexible PET substrate, and by studying the changes of resistance and phonon vibration modes of the homogeneous phase of M1-M2 in the radial distribution, they found the M1-M2 and M2-M1 modes under the action of stress in different directions, and the sensor showed good sensitivity to the stress direction.

In recent years, neural networks as sensor integration applications have developed rapidly. Li et al.<sup>[166]</sup> built a typical ANN to test the MNIST datebase based on a designed VO<sub>2</sub>/mica flexible sensing module for UV light writing (oxygen effusion) and gated electrolyte erasure (oxygen insertion). As shown in the **Figure 16**, the whole system adopts a near-sensor computing architecture, and the image information can be read from the sensor unit through the voltage and transmitted to the ANN classifier to realize the training of artificial neural networks.

At present,  $VO_2$  has been successfully designed with a variety of sensors and has shown good sensing performance. At the same time,  $VO_2$  sensors can be modified in a variety of ways, so the corresponding sensors have strong environmental adaptability. In short,  $VO_2$  is a material with applicability in the field of sensors, with some market prospects and development potential.

## 6.3. Smart Windows

 $VO_2$  is an excellent thermochromic and electrochromic material with great application potential in the field of smart windows. Through thin film fabrication technology,  $VO_2$  smart windows can actively or passively respond according to the environment and needs, modulating transmitted light, which has strong application values. Since 2003, when Kato et al.<sup>[168]</sup> first proposed the concept of  $VO_2$  smart windows, the research of  $VO_2$  smart windows has made great progress. The following mainly introduces the development of  $VO_2$  smart windows from the aspects of optimization technology and performance.

The most common adjustment method of  $VO_2$  smart window is thermal adjustment based on thermochromic properties, generally the critical temperature of  $VO_2$  film thermochromic is 68 °C, but through elemental doping, interface effect and www.advancedsciencenews.com



8

NFC Chip

LDO Amplifier

Sensor

Loop Coil



Figure 15. a) Schematic diagram of the circuit design; b) Schematic of the device: stacks represent different layers of the device; c) Optical photograph of the fabricated device. Reproduced with permission.[165] Copyright 2021, TAYLOR & FRANCIS.

Circuits

external field action can greatly reduce the phase change temperature of VO<sub>2</sub>, or even reduce to room temperature, the film shows excellent ambient light modulation ability, to achieve passive adjustment at room temperature. In Section 5, the excellent modification effect of doping on VO<sub>2</sub> films, especially large particle elements such as W, can easily reduce T<sub>C</sub> to room temperature.<sup>[32,130b,169]</sup> However, the optical modulation ability of W-doped VO<sub>2</sub> thin films is not good enough, so some individuals have proposed the mechanism of elemental co-doping,<sup>[139,141,170]</sup> using low-valence ions to widen the optical band gap, inhibit the absorption of visible light, and improve the transmittance of visible light. However, co-doping still cannot meet the ultra-high transparency of smart windows, which greatly affects the application process of VO<sub>2</sub> smart windows.

In subsequent work, scientists found that the introduction of polymers could improve the optical performance of smart windows. According to the mixing rule of pure components, the extinction coefficient of VO<sub>2</sub>/polymer composite film is between pure VO<sub>2</sub> particles and polymers, because many polymers are almost transparent to visible light, so the transmittance of composite films compared with pure VO<sub>2</sub> films or doped films has been significantly improved.<sup>[171]</sup> Based on this mixing, the composite film can also change the unfavorable yellow color of the original VO<sub>2</sub> and improve the aesthetics of the film.<sup>[171a,172]</sup>

However, the aggregation of VO<sub>2</sub> NPs in polymers increases absorption and scattering, which in turn deteriorates the optical properties of VO<sub>2</sub> composite films.<sup>[171c]</sup> The interaction between oppositely charged groups in hydrophilic polymers with suitable viscosity can improve the dispersion of VO<sub>2</sub> NPs and improve the uniformity of film formation, inhibit polymer conjugation and coffee-ring effect, and improve the visible light transmittance and infrared modulation ability of the film.<sup>[171c,173]</sup> As an example, Zomaya et al.<sup>[3d]</sup> tested the dispersion of VO<sub>2</sub> in P4VP, and the results showed that in the P4VP system, VO<sub>2</sub> has the highest degree of dispersion due to the coordination of VO<sub>2</sub> and pyridine ring, and that the P4VP/VO<sub>2</sub> films exhibited satisfactory visible light transmittance and infrared modulation by adjusting the polymer concentration and film thickness.

Moreover, the presence of polymers makes it easier to produce "discontinuous" coatings (e.g., porous coatings or etched films) that increase light transmittance without decreasing infrared modulation.<sup>[172,174]</sup> Among them, the increase in porosity improves the modulation of film transmittance and solar transmittance is ascribed to interfacial scattering that limit direct surface reflection.<sup>[172,174b,175]</sup> Etching and self-patterning increase the transmittance of the composite film through the anti-reflection effect.[172,176]







**Figure 16.** Schematic diagram of the near-sensor computing architecture for multitasking, including the recognition of MNIST dataset and edgeenhancement processing. Two Sobel convolution kernels were used for vertical and horizontal edge detections, respectively, and the Laplace convolution kernel was used to detect edges in all directions. Reproduced with permission.<sup>[166]</sup> Copyright 2022, WILEY-VCH.

Studies have shown that VO<sub>2</sub> NPs in metallic state can undergo surface plasmon resonance (SPR), which affects scattering and absorption.<sup>[171b,174a,177]</sup> The homogeneous dispersion of VO<sub>2</sub> NPs by polymers can minimize large scattering centers that do not exhibit the desired plasmon resonance, and maintain high absorption of metal nanoparticles at resonance (at  $\approx 1.2 \,\mu$ m), resulting in a decrease in infrared transmittance at the same spectral position and an increase in modulation ability. In addition, the polymer gives the film good tensile properties, which can change the dispersion of VO<sub>2</sub> NPs and the influence of plasmon resonance, and the spacing between NPs can be changed or voids can be introduced after stretching, so as to change the optical transparency of the film and obtain more ideal spectral properties. In addition, the polymer can introduce the advantages of VO<sub>2</sub> NPs size and shape on surface plasmon resonance tuning into the design of smart windows, promising the highest performing thermochromic windows.<sup>[171b]</sup> Common VO<sub>2</sub> polymer film materials include PVP,<sup>[130a,178]</sup> PMMA,<sup>[179]</sup> P4VP<sup>[3d]</sup> and PNIPAm.<sup>[144,180]</sup> Acrylic and polyurethane (PU) are also commonly used as host polymer materials for VO<sub>2</sub>/polymer thermochromic films.<sup>[172]</sup> The properties of the films prepared by different polymers are different.

Unlike the polymer tested above, PNIPAm has phase change characteristics, and the phase change temperature is low: a large number of hydrogen bonds are formed between water and PNI-PAm molecular chains, once the temperature exceeds the critical solution temperature (LCST), water molecules will be released from PNIPAm macromolecules, and the polymer collapses, resulting in a strong optical contrast between PNIPAm and water, and light scattering on the interface between PNI-PAm particles and surrounding water, resulting in a decrease in transmittance.<sup>[144]</sup>

For example, in 2021, Zhang et al.<sup>[144]</sup> prepared a  $V_{0.8}W_{0.2}O_2$ @SiO<sub>2</sub> doped [poly(N-isopropyl acrylamide), PNI-PAm] (VSP) microgel film with ultra-high light transmittance and optical modulation ability, with transmittance of 92.48% in the visible light region, 77.20% solar modulation efficiency, and phase transition temperature as low as 30 °C, showing strong contrast at room temperature. In addition, Feng et al.<sup>[180a]</sup> tried to add additional HPC and successfully prepared a W-VO<sub>2</sub>/PNIPAm-HPC hydrogel membrane with T<sub>lum</sub> of 87.16%,  $\Delta T_{sol}$  of 65.71%, and critical solution temperature (LCST) of 29°C. As shown in Figure 17b–f, the HPC network prevents volume shrinkage of PNIPAm phase transition through hydrogen bond interaction and high crosslinking density between PNIPAm and HPC polymer chains, improving the reversibility and durability of smart windows.

While improving the optical performance of smart windows, service life is also a key research direction.  $VO_2$  oxidizes slowly at room temperature, and has poor moisture and oxygen resistance. In order to achieve a high-quality smart window with a long life, it is necessary to hinder the oxidation of  $VO_2$  through preparation technology. Although the existence of the polymer can block a certain amount of moisture and oxygen, due to the large surface energy of  $VO_2$ , it is easy to agglomerate, and has poor affinity with the organic matrix, forming interfacial gaps. Over time, moisture

CIENCE NEWS www.advancedsciencenews.com www.advelectronicmat.de (a) OH TEOS, NH4OH, KH-570 H.O. ethanol VO, VO,@SiO, Step 4: dispersion in PU Step 1: PVP pretreatment Step 2: shell growth Step 3: surface modification (b) (c) ¥ (R-Hor-CH2CH(OH)CH3) Glass slide W-VO2/PNIPAm-HPC thermochromic hydrogel HPC PNIPA (d)NIR Smart window prototype stirring 20 % T<LCST PNIPAm T>LCST HPC W-VO2/PNIPAm-HPC thermochromic hydr Hydrogen bonding N-isopropyl acrylamide N. N'-methylene-bisacrylamide 0 Initiator O W-VO W-VO2 WWW Hydrogen bonding нрс Catalyst PNIPAm Phase transition (g) (e) Heating PNIPAm MBA



40 °C

HPC

Hydrogen bonding

water

Amorphous V<sub>2</sub>O<sub>5</sub>

Substrate

and oxygen will still invade, greatly affecting the performance of smart windows.<sup>[179a]</sup> The core-shell coating can reduce the surface energy of VO<sub>2</sub>, improve the dispersion and compatibility of  $VO_2$  in the polymer (Figure 17a), and enhance the durability of smart windows.<sup>[172,179a,b,181]</sup> However, the core-shell structure is prone to crack due to the transformation of VO2 lattice structure, and increasing the molecular weight of the polymer and crosslinking the adjacent polymer can well prevent the diffusion of gas in the polymer.<sup>[179b,183]</sup>

20 °C

In addition, setting the protective layer is also an efficient way to block water oxyzen and improve the lifespan of windows. Vu et al.<sup>[182]</sup> first formed a unique VO<sub>2</sub> nanorod embedded structure by introducing seeding to guide growth during the reaction sputtering process, and then formed a  $V_2O_5/VO_2$  thermochromic composite film (as shown in the Figure 17 g), the presence of  $V_2O_5$  reduced the lattice mismatch of the amorphous surface of VO<sub>2</sub> crystal and blocked water oxygen, thereby greatly slowing down the oxidation process of VO<sub>2</sub>, and finally tested the life of the smart window was as high as 33 years. Similarly, Li et al.<sup>[184]</sup> designed a  $V_2O_3/VO_2/V_2O_5$  structure, which also uses the  $V_2O_5$ layer to hinder the oxidation of VO<sub>2</sub>, and the service life of the window can reach 20 years after accelerated experimental tests. In addition, the use of core-shell coating can greatly slow down the oxidation process of VO<sub>2</sub> and ensure the optical properties of the prepared thin film.<sup>[181,185]</sup>

Compared with thermochromic smart windows, VO<sub>2</sub> electrochromic smart windows can actively adjust the window function through electrical control, and have a strong degree of

**PNIPAm** 

**PNIPAm-HPC** 

(f)

Shrinking

Heating

Shrinking

OH



adjustment freedom. Nakano et al.<sup>[35a]</sup> used FET structure to study the electrochromic characteristics of VO<sub>2</sub>, and found that the modulation efficiency of the film in the infrared band is little high, pointing out the development potential of VO<sub>2</sub> in the field of energy-saving smart windows. Chen et al.<sup>[69]</sup> studied the optical performance change of VO<sub>2</sub> phase transition by gating voltage control H doping, and realized an electronically controlled smart window with a solar modulation capacity of 26.5% while maintaining a visible luminous transmittance of 70.8%.

However, VO<sub>2</sub> electrochromic performance is inferior, so some researchers combine the thermochromic properties of VO<sub>2</sub> with the electrochromic properties of other materials (such as WO<sub>3</sub>) to construct a smart window that can respond to both electrical and thermal, realizing the integration of active and passive response. For example, Jia et al.<sup>[186]</sup> added Li<sup>+</sup>/Al<sup>3+</sup> composite solid electrolyte between the thermochromic VO<sub>2</sub> layer and the electrochromic WO<sub>3</sub> layer. The device can achieve independent modulation of visible and near-infrared light through active response to voltage, passive response to temperature, or a combination of both, and obtain four reversible functional modes. Lee et al.<sup>[187]</sup> also used WO<sub>3</sub> and VO<sub>2</sub> materials to prepare flexible electro-thermal intelligent windows on the basis of WO<sub>3</sub> EC and VO<sub>2</sub> TC devices, which provided ideas for the development of flexible multi-functional smart windows in the future.

Now VO<sub>2</sub> smart windows have developed relatively mature, windows as a heat exchange medium in most environments, efficient light modulation ability can make it have efficient energy-saving effects,<sup>[188]</sup> coupled with the breakthrough of service life, which makes VO<sub>2</sub> in indoor home, car windows and other fields of industrialization accelerated, becoming a classic material from laboratory to market.

## 6.4. Other Applications

In addition to the above application range,  $VO_2$  is also used in the design of some other optical and electrical devices due to its special phase change properties. For example, FETs are a class of semiconductor devices that control the output loop current by controlling the electric field effect of the input loop. Because  $VO_2$  can control phase transition through electric field, it has unique attraction in the field of circuit switching elements such as FET, and achieves performance optimization on the basis of traditional FETs and realizes a series of phase change FETs.

For example, in 2015, Shukla et al.<sup>[16b]</sup> designed a hyper-FET, the schematic is shown in the **Figure 18**a, through the given drain-to-source voltage ( $V_{DS}$ ) and gate bias  $V_{GS}$  to change the  $I_{DS}$ , trigger a sudden phase transition of VO<sub>2</sub>, which in turn leads to a sudden  $I_{DS}$  mutation, so that the device has a steep reversible switching behavior, and the output characteristic curve shows excellent  $I_{DS}$  saturation behavior (Figure 18b). This I-V feedback behavior results in a negative differential resistance (Figure 18c), which is equivalent to creating an internal amplifier that enhances performance over traditional field-effect transistors. In 2019, Dasgupta et al.<sup>[189]</sup> used Verilog-A to build a physically compact model similar to Nikhil Shukla, using self-heating to capture temperature-dependent multidomain switching behavior, reaching similar conclusions to Shukla et al.

In the same year, Yamamoto et al.<sup>[190]</sup> used the transistor structure to study the contact characteristics of  $VO_2/MOS_2$  and  $VO_2/WSe_2$  heterojunctions in the transistor structure, and observed that the high contact resistance at the contact of  $VO_2$ ,  $MOS_2$  and  $WSe_2$  due to the formation of the interface barrier, which is crucial for the research and application of high-performance phase change FETs. In addition, it has been previously reported that doping can effectively reduce the barrier, thereby effectively reducing the contact resistance.<sup>[191]</sup>

In addition, VO<sub>2</sub> also has related applications in memory devices, and the design principle is similar to that of neuronal sensors. For example, Bae et al.<sup>[9]</sup> first reported a two-terminal memristor memory based on a single VO<sub>2</sub> nanowire, which used the special hysteresis characteristics of the VO<sub>2</sub> I-V curve to maintain thermal stability in the hysteresis region through Joule heating generated by a specific bias voltage, and then used electrical pulses to achieve resistance switching.

In 2021, Jung et al.<sup>[192]</sup> first reported a VO<sub>2</sub> light-addressable non-volatile memory at room temperature, which can be written by a low-power optical pump, read out by voltage oscillations between the insulator-metallic state after the input bias current, and can also reset the memory by applying a smaller bias current, which provides ideas for the design of light-addressed nonvolatile devices.

Finally, vanadium dioxide is a promising microactuator material due to its high modulus of elasticity, large amplitude and high volumetric work density in the transition between the insulating M1/M2 and metal (R) phases.<sup>[16a,193]</sup>

In 2019, Shi et al.<sup>[8b]</sup> used the VO<sub>2</sub> M1-R phase change to design and fabricate tungsten-doped single-crystalline actuator that can work at room temperature for the first time, as shown in the **Figure 19**, unlike the bimorph actuator, the singlecrystalline actuator uses the laterally asymmetric strain/domain distribution caused by the internal inhomogeneity gradient for bending actuating, and finally achieves a maximum energy conversion efficiency is  $\approx 0.83\%$ , and the curvature  $\Delta\kappa m$  is  $\approx 2.5 \times 10^4$  m<sup>-1</sup>, which is greatly optimized compared with the bimorph actuator.<sup>[194]</sup> It was also found that the curvature had an almost linear relationship with ambient temperature before SCVAs reached their maximum curvature, which gave high sensitivity to the continuous and precise modulation of therm-driven bending ((0.125–0.25)×10<sup>4</sup> m<sup>-1</sup> K<sup>-1</sup>).

Later, Zhang et al.<sup>[16a]</sup> obtained M2 phase VO<sub>2</sub> NWs single crystal by thermal evaporation, using the method of in situ electrical-force coupling test, the actuation stress of the microactuator driven by VO<sub>2</sub> NWs phase transition is quantitatively studied, and the results showed that the phase change stress could reach 2.09 GPa and the volumetric work density could reach 15.9 J cm<sup>-3</sup>, showing superior driving ability than VO<sub>2</sub> (M1).

Highly efficient microactuators are critical in microelectromechanical systems (MEMS), micromanipulation, micromechanical switches, microrobotics, and more.  $VO_2$  improves microactuators due to its excellent actuation characteristics, and  $VO_2$ -based microactuators have great application value and promote the development of microactuators.

In short, due to its unique phase change characteristics and electrochemical characteristics,  $VO_2$  is used in the preparation of optical and electrical devices, and has application potential in the field of new devices. However,  $VO_2$  has some mysteries that

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**Figure 18.** a) Schematic of a hyper-FET consisting of a two-terminal VO<sub>2</sub> device; b)  $I_{DS}$ –V<sub>GS</sub> transfer characteristics of the hyper-FET exhibiting abrupt and reversible modulation of the channel current  $I_{DS}$  as a function of the gate-source voltage  $V_{GS}$ . The abrupt turn-ON and turn-OFF of the hyper-FET corresponds to the IMT and MIT in VO<sub>2</sub>, respectively; c) Current versus voltage characteristics of the VO<sub>2</sub> device with (red) and without (blue) the MOSFET in series, illustrating the electrically triggered abrupt IMT. Reproduced with permission.<sup>[16b]</sup> Copyright 2015, Springer Nature.

have not yet been solved, and its practical application process is affected by the disadvantages of poor resistance to water, oxygen and high temperature, and high light absorption. More efforts are needed to promote the commercial application process of VO<sub>2</sub>.

## 7. Summary and Outlook

In summary, based on the unique MIT behavior,  $VO_2$  material is an excellent functional material with great application potential in the field of optical and electrical devices. In this review, we first summarize the mechanism explanations of  $VO_2$ insulator-metal phase transition, during which the lattice structure and electronic structure of  $VO_2$  change significantly, making the  $VO_2$  mechanism still questionable. At present, the Peierls mechanism, Mott mechanism and Mott-Peierls mechanism of phase transition have their corresponding experimental proofs, so it is speculated that the  $VO_2$  phase transition mechanism may be related to experimental conditions, and the specific explanation needs to be further studied. We then present the optical and electrical properties caused by phase transition, in which we summarize the bandgap explanations for changes in optical properties in existing reports. The hysteresis accompanied by changes in physical properties has always been the focus of VO<sub>2</sub> material, and we specially summarize this part to point out the research progress of hysteresis phenomenon and its application value in different application conditions. At present, there are few reports on the elimination of hysteresis. Doping and particle size have been proved to be effective in reducing VO<sub>2</sub> hysteresis, but how to effectively eliminate VO<sub>2</sub> hysteresis still needs further exploration.

As a strongly correlated material,  $VO_2$  can be modulated by thermal, electrical, optical, strain, magnetic and doping. There is a crossover of mechanisms behind different modulation methods, such as thermal modulation and electro-joule heating. Different from the previous review of regulatory methods, this paper mainly summarizes various regulatory methods from the perspective of application, and provides a detailed overview of the corresponding control structures (electrical, optical and strain). ADVANCED SCIENCE NEWS \_\_\_\_\_\_ www.advancedsciencenews.com



Figure 19. Schematics of typical  $VO_2$ /supporting layer (SL) bimorph actuator and the proposed single-crystalline  $VO_2$  actuator. a) T (phase transition temperature) distribution and b) corresponding bending principles of bimorph actuator (left) and single-crystalline actuator (right). Reproduced with permission.<sup>[8b]</sup> Copyright 2019, WILEY-VCH.

In addition, magnetron is a new control method that has been studied in recent years, which triggers  $VO_2$  phase transition or affects  $VO_2$  phase transition characteristics through direct or indirect action of magnetic field, as a non-contact control method, it has deep research significance. However, the thermal generation and triggering mechanism of some  $VO_2$ -based devices are still controversial, which affects the preparation and development of devices. The optimization of device structure can avoid the generation of unnecessary heat quantity and other influencing factors, which has inspirations for the design of  $VO_2$ -based devices in the future.

In addition, this paper focuses on doping, as a special "modification", it has an excellent modification effect on VO<sub>2</sub> and has a wide range of applications in the field of intelligent coatings. Finally, the application process of VO<sub>2</sub> in recent years has been intensely rapid, and it has achieved remarkable results in popular devices such as smart windows, sensors, terahertz modulators and FETs. As a classic application of VO<sub>2</sub>, the smart windows have been greatly improved the optical performance and service life by doping, introducing polymer, core-shell coating, setting protective layer and other preparation processes. These methods have guiding significance for the life improvement and performance optimization of other devices. In addition, throughout a variety of VO<sub>2</sub> applications, ultrafast control methods such as electronic control and optical control will be extremely potential control methods, and will be a significant updating for many optical and electrical devices. This paper summarizes the progress of the above  $VO_2$ -based devices in recent years, points out the key breakthroughs in  $VO_2$  applications in the future and new potential applications, and has a certain guiding role in the process of  $VO_2$  application.

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## **Conflict of Interest**

The authors declare no conflict of interest.

## Keywords

metal-insulator phase transition, modulation methods, optical and electrical application, vanadium dioxide

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- [1] F. J. Morin, Phys. Rev. Lett. 1959, 3, 34.
- [2] a) V R. Morrison, R. P. Chatelain, K L. Tiwari, A. Hendaoui, A. Bruhács, M. Chaker, B J. Siwick, *Science* 2014, *346*, 445; b) J D. Budai, J. Hong, M E. Manley, E D. Specht, C W. Li, J Z. Tischler, D L. Abernathy, A H. Said, B M. Leu, L A. Boatner, R J. Mcqueeney, O. Delaire, *Nature* 2014, *515*, 535.
- [3] a) S. Azad, D. Gajula, G. Koley, *Thin Solid Films* 2022, *742*, 139055;
  b) S. Azad, D. Gajula, N. Sapkota, A. Rao, G. Koley, *Micromachines* 2022, *13*, 812; c) J. Jeong, N. Aetukuri, T. Graf, T. D. Schladt, M. G. Samant, S. S. P. Parkin, *Science* 2013, *339*, 1402; d) D. Zomaya, W Z. Xu, B. Grohe, S. Mittler, P A. Charpentier, *ACS Appl. Nano Mater.* 2020, *3*, 6645; e) C. Ling, Z. Zhao, X. Hu, J. Li, X. Zhao, Z. Wang, Y. Zhao, H. Jin, *ACS Appl. Nano Mater.* 2019, *2*, 6738; f) K. Liu, S. Lee, S. Yang, O. Delaire, J. Wu, *Mater. Today* 2018, *21*, 875.
- [4] a) M. Liu, E. Plum, H. Li, S. Li, Q. Xu, X. Zhang, C. Zhang, C. Zou,
   B. Jin, J. Han, W. Zhang, Adv. Funct. Mater. 2021, 31, 2010249; b) I.
   Latella, O. Marconot, J. Sylvestre, L G. Fréchette, P. Ben-Abdallah,
   Phys. Rev. Appl. 2019, 11, 024004.
- [5] a) J. Del Valle, N M. Vargas, R. Rocco, P. Salev, Y. Kalcheim, P N. Lapa, C. Adda, M.-H. Lee, P Y. Wang, L. Fratino, M J. Rozenberg, I K. Schuller, *Science* 2021, *373*, 907; b) Y. Kalcheim, A. Camjayi, J. Del Valle, P. Salev, M. Rozenberg, I K. Schuller, *Nat. Commun.* 2020, *11*, 2985; c) M. Nakano, K. Shibuya, D. Okuyama, T. Hatano, S. Ono, M. Kawasaki, Y. Iwasa, Y. Tokura, *Nature* 2012, *487*, 459.
- [6] a) D. Singh, C. S. Yadav, B. Viswanath, *Mater. Lett.* 2017, *196*, 248;
  b) Y H. Matsuda, D. Nakamura, A. Ikeda, S. Takeyama, Y. Suga, H. Nakahara, Y. Muraoka, *Nat. Commun.* 2020, *11*, 3591.
- [7] a) Ge Li, D. Xie, H. Zhong, Z. Zhang, X. Fu, Q. Zhou, Q. Li, H. Ni, J. Wang, Er-J Guo, M. He, C. Wang, G. Yang, K. Jin, C. Ge, *Nat. Commun.* 2022, *13*, 1729; b) S. Wall, S. Yang, L. Vidas, M. Chollet, J M. Glownia, M. Kozina, T. Katayama, T. Henighan, M. Jiang, T A. Miller, D A. Reis, L A. Boatner, O. Delaire, M. Trigo, *Science* 2018, *362*, 572; c) A. S. Johnson, D. Perez-Salinas, K. M. Siddiqui, S. Kim, S. Choi, K. Volckaert, P. E. Majchrzak, S. Ulstrup, N. Agarwal, K. Hallman, R. F. Haglund, C. M. Gunther, B. Pfau, S. Eisebitt, D. Backes, F. Maccherozzi, A. Fitzpatrick, S. S. Dhesi, P. Gargiani, M. Valvidares, N. Artrith, F. de Groot, H. Choi, D. Jang, A. Katoch, S. Kwon, S. H. Park, H. Kim, S. E. Wall, *Nat. Phys.* 2023, *19*, 215.
- [8] a) D. Lee, J. Lee, K. Song, F. Xue, Si-Y Choi, Y. Ma, J. Podkaminer, D. Liu, S.-C. Liu, B. Chung, W. Fan, S. J. Cho, W. Zhou, J. Lee, L.-Q. Chen, S Ho Oh, Z. Ma, C.-B. Eom, *Nano Lett.* **2017**, *17*, 5614; b) R. Shi, X. Cai, W. Wang, J. Wang, D. Kong, N. Cai, P. Chen, P. He, Z. Wu, A. Amini, N. Wang, C. Cheng, *Adv. Funct. Mater.* **2019**, *29*, 1900527.
- [9] S.-H. Bae, S. Lee, H. Koo, L. Lin, B. H. Jo, C. Park, Z. L. Wang, Adv. Mater. 2013, 25, 5098.
- [10] a) H.-T. Kim, B.-G. Chae, D.-H. Youn, S.-L. Maeng, G. Kim, K.-Y. Kang, Y.-S. Lim, *New J. Phys.* **2004**, *6*, 52; b) J. I. Sohn, S. N. Cha, S. B. Son, J. M. Kim, M E. Welland, W-Ki Hong, *Nanoscale* **2017**, *9*, 8200.
- [11] a) S. Chen, Xi J Wang, L. Fan, G. Liao, Y. Chen, W. Chu, Li Song, J. Jiang, C. Zou, *Adv. Funct. Mater.* **2016**, *26*, 3532; b) X. Deng, Yi-F Zhao, Ni Zhong, F-Yu Yue, R. Huang, H. Peng, X.-D. Tang, P.-H. Xiang, Y.-H. Chu, C.-G. Duan, *Adv. Electron. Mater.* **2019**, *6*, 1900742.
- [12] a) N. Smieszek, S. Joshi, V. Chakrapani, *Appl. Phys. Lett.* 2022, *120*, 062102; b) K. Liu, D. Fu, J. Cao, J. Suh, K X. Wang, C. Cheng, D. F Ogletree, H. Guo, S. Sengupta, A. Khan, C. W. Yeung, S. Salahuddin, M M. Deshmukh, J. Wu, *Nano Lett.* 2012, *12*, 6272.
- [13] a) M. M. Qazilbash, M. Brehm, B.-G. Chae, P.-C. Ho, G. O. Andreev, B.-J. Kim, S. J. Yun, A. V. Balatsky, M. B. Maple, F. Keilmann, H.-

T. Kim, D. N. Basov, *Science* **2007**, *318*, 1750; b) G. Stefanovich, A. Pergament, D. Stefanovich, *J. Phys.: Condens. Matter* **2000**, *12*,

[14] R M. Wentzcovitch, W W. Schulz, P B. Allen, *Phys. Rev. Lett.* **1994**, 72, 3389.

8837.

- [15] a) S. Chen, J. Liu, H. Luo, Y. Gao, J. Phys. Chem. Lett. 2015, 6, 3650;
   b) T. Yao, X. Zhang, Z. Sun, S. Liu, Y. Huang, Yi Xie, C. Wu, X. Yuan,
   W. Zhang, Z. Wu, G. Pan, F. Hu, L. Wu, Q. Liu, S. Wei, Phys. Rev. Lett. 2010, 105, 226405.
- [16] a) Y.-Q. Zhang, K. Chen, H. Shen, Y.-C. Wang, M. N. Hedhili, X. Zhang, Ju Li, Z.-W. Shan, *Nano Res.* 2021, *14*, 4146; b) N. Shukla, A V. Thathachary, A. Agrawal, H. Paik, A. Aziz, D G. Schlom, S. K. Gupta, R. Engel-Herbert, S. Datta, *Nat. Commun.* 2015, *6*, 7812; c) Qi Hao, W. Li, H. Xu, J. Wang, Y. Yin, H. Wang, L. Ma, F. Ma, X. Jiang, O G. Schmidt, P K. Chu, *Adv. Mater.* 2018, *30*, 1705421; d) X. Zhao, J. Lou, X. Xu, Y. Yu, G. Wang, J. Qi, L. Zeng, J. He, J. Liang, Y. Huang, D. Zhang, C. Chang, *Adv. Opt. Mater.* 2022, *10*, 2102589; e) T. Wang, J. He, J. Guo, X. Wang, S. Feng, F. Kuhl, M. Becker, A. Polity, P J. Klar, Y. Zhang, *Opt. Express* 2019, *27*, 20347; f) E. Strelcov, Y. Lilach, A. Kolmakov, *Nano Lett.* 2009, *9*, 2322.
- [17] a) A. Tselev, I. A. Luk'yanchuk, I. N. Ivanov, J. D. Budai, J. Z. Tischler,
  E. Strelcov, A. Kolmakov, S. V. Kalinin, *Nano Lett.* 2010, *10*, 4409;
  b) S. S. Majid, D. K. Shukla, F. Rahman, S. Khan, K. Gautam, A. Ahad, S. Francoual, R. J. Choudhary, V. G. Sathe, J. Strempfer, *Phys. Rev. B* 2018, *98*, 075152; c) K. L. Gurunatha, S. Sathasivam, J. Li, M. Portnoi, I P. Parkin, I. Papakonstantinou, *Adv. Funct. Mater.* 2020, *30*, 2005311
- [18] a) L. Chen, Y. Liu, K. Yang, P. Lan, Y. Cui, H. Luo, B. Liu, Y. Gao, *Comput. Mater. Sci.* 2019, 161, 415; b) J B. Goodenough, *J. Solid State Chem.* 1971, 3, 490; c) N B. Aetukuri, A X. Gray, M. Drouard, M. Cossale, Li Gao, A H. Reid, R. Kukreja, H. Ohldag, C A. Jenkins, E. Arenholz, K P. Roche, H A. Dürr, M G. Samant, S S. P. Parkin, *Nat. Phys.* 2013, 9, 661; d) J. Sang, T. Zheng, L. Xu, X. Zhou, S. Tian, J. Sun, X. Xu, J. Wang, S. Zhao, Y. Liu, *J. Alloys Compd.* 2021, 876, 160208.
- [19] Y. Ishiwata, S. Suehiro, M. Hagihala, X. G. Zheng, T. Kawae, O. Morimoto, Y. Tezuka, Phys. Rev. B 2010, 82, 115404.
- [20] a) H.-T. Kim, B.-J. Kim, Y. W. Lee, B.-G. Chae, S. J. Yun, K.-Y. Kang, *Phys. C: Supercond.* 2007, *460*, 1076; b) Y. G. Liang, S. Lee, H. S. Yu, H. R. Zhang, Y. J. Liang, P. Y. Zavalij, X. Chen, R. D. James, L. A. Bendersky, A. V. Davydov, X. H. Zhang, I. Takeuchi, *Nat. Commun.* 2020, *11*, 3539; c) D. Lee, B. Chung, Y. Shi, G.-Y. Kim, N. Campbell, F. Xue, K. Song, S.-Y. Choi, J. P. Podkaminer, T. H. Kim, P. J. Ryan, J.-W. Kim, T. R. Paudel, J.-H. Kang, J. W. Spinuzzi, D. A. Tenne, E. Y. Tsymbal, M. S. Rzchowski, L. Q. Chen, J. Lee, C. B. Eom, *Science* 2018, *362*, 1037.
- [21] Z. Shao, X. Cao, H. Luo, P. Jin, NPG Asia Mater. 2018, 10, 581.
- [22] a) S. Biermann, A. Poteryaev, A. I. Lichtenstein, A. Georges, *Phys. Rev. Lett.* 2005, *94*, 026404; b) A. Zylbersztejn, N. F. Mott, *Phys. Rev. B* 1975, *11*, 4383.
- [23] H.-T. Kim, Y. W. Lee, B.-J. Kim, B.-G. Chae, S. J. Yun, K.-Y. Kang, K.-J. Han, Ki-Ju Yee, Y.-S. Lim, *Phys. Rev. Lett.* **2006**, *97*, 266401.
- [24] B.-J. Kim, Y. W. Lee, S. Choi, J.-W. Lim, S. J. Yun, H.-T. Kim, T-Ju Shin, H.-S. Yun, *Phys. Rev. B* 2008, *77*, 235401.
- [25] W.-T. Liu, J. Cao, W. Fan, Z. Hao, M C. Martin, Y. R. Shen, J. Wu, F. Wang, *Nano Lett.* **2011**, *11*, 466.
- [26] C.-Y. Kim, T. Slusar, J. Cho, H.-T. Kim, ACS Appl. Electron. Mater. 2021, 3, 605.
- [27] Y. Meng, K. Huang, Z. Tang, X. Xu, Z. Tan, Q. Liu, C. Wang, B. Wu, C. Wang, J. Cao, Appl. Surf. Sci. 2018, 427, 304.
- [28] X. Cheng, Q. Gao, K. Li, Z. Liu, Q. Liu, Q. Liu, Y. Zhang, B. Li, Nanomaterials 2019, 9, 2061.
- [29] a) G. Wei, X. Lin, Z. Si, D. Wang, X. Wang, X. Fan, K. Deng, K. Liu, K. Jiang, Na Lei, Y. Chen, S. Mangin, E. Fullerton, W. Zhao, Adv. Quantum Technol. 2020, 3, 1900104; b) L. Pellegrino, N. Manca, T. Kanki,



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**ADVANCED** SCIENCE NEWS

H. Tanaka, M. Biasotti, E. Bellingeri, A. S. Siri, D. Marré, *Adv. Mater.* **2012**, *24*, 2929.

- [30] A. S. Barker, H. W. Verleur, H. J. Guggenheim, Phys. Rev. Lett. 1966, 17, 1286.
- [31] X. Geng, T. Chang, J. Fan, Yu Wang, X. Wang, Y. Sun, P. Selvarajan, C. Liu, C-Ho Lin, X. Wang, J. Yang, Z. Cheng, K. Kalantar-Zadeh, X. Cao, D. Wang, A. Vinu, J. Yi, T. Wu, ACS Appl. Mater. Interfaces 2022, 14, 19736.
- [32] X. Wang, L. Chen, H. Lu, W. Fang, H. Li, W. Yin, M. Li, Y. Lu, P. Li, Y. He, *Appl. Phys. Lett.* **2021**, *118*, 192102.
- [33] C. Ji, Z. Wu, L. Lu, X. Wu, J. Wang, X. Liu, H. Zhou, Z. Huang, J. Gou, Y. Jiang, J. Mater. Chem. C 2018, 6, 6502.
- [34] a) J. Yang, D. Li, X. Wang, H. Jin, J. Li, *Appl. Surf. Sci.* 2022, 600, 154074; b) P.-P. Wang, Y.-Z. Zhang, M.-D. Peng, Y.-L. Zhang, L.-N. Wu, Y.-Z. Cao, L.-X. Song, *Acta Phys. Sin.* 2016, 65, 127201.
- [35] a) M. Nakano, K. Shibuya, N. Ogawa, T. Hatano, M. Kawasaki, Y. Iwasa, Y. Tokura, *Appl. Phys. Lett.* 2013, 103, 153503; b) T. G. Sánchez, S. Amador-Alvarado, Y. Kumar, D. Ariza-Flores, M. A. Basurto-Pensado, V. Agarwal, *Mater. Lett.* 2022, 323, 132541.
- [36] S-Yi Li, N R. Mlyuka, D. Primetzhofer, A. Hallén, G. Possnert, G A. Niklasson, C G. Granqvist, Appl. Phys. Lett. 2013, 103, 161907.
- [37] E E. Chain, Appl. Opt. **1991**, 30, 2782.
- [38] W. Xu, Z. Wu, Z. Xiang, J. Gou, X. Dong, J. Wang, Y. Jiang, Opt. Mater. 2021, 117, 111142.
- [39] T. V. Son, K. Bulmer, A. Haché, J.-F. Bisson, Opt. Commun. 2023, 530, 129130.
- [40] a) X. Xu, X. He, H. Wang, Q. Gu, S. Shi, H. Xing, C. Wang, J. Zhang, X. Chen, J. Chu, *Appl. Surf. Sci.* **2012**, *261*, 83; b) T. Chang, Y. Zhu, J. Huang, H. Luo, P. Jin, X. Cao, *Sol. Energy Mater. Sol. Cells* **2021**, *219*, 110799.
- [41] G. B. Olson, M. Cohen, Metall. Trans. A 1976, 7, 1897.
- [42] a) T. Zheng, J. Sang, Z. Hua, L. Xu, X. Xu, C. Wang, B. Wu, J. Alloys Compd. 2021, 865, 158755; b) R. Molaei, R. Bayati, F. Wu, J. Narayan, J. Appl. Phys. 2014, 115, 164311; c) J. Narayan, V. M. Bhosle, J. Appl. Phys. 2006, 100, 103524.
- [43] B. Li, S. Tian, Z. Wang, B. Liu, X. Gong, X. Zhao, Appl. Surf. Sci. 2021, 568, 150959.
- [44] a) K. Nishikawa, M. Yoshimura, Y. Watanabe, J. Appl. Phys. 2021, 129;
  b) A. Ainabayev, D. Mullarkey, B. Walls, D. Caffrey, K. Zhussupbekov,
  A. Zhussupbekova, C. Ilhan, A. Kaisha, P. Biswas, A. Tikhonov, O. Murtagh, I. Shvets, ACS Appl. Nano Mater. 2023, 6, 2917.
- [45] W. Zeng, H. Lai, T. Chen, Y. Lu, Z. Liang, T. Shi, Ke Chen, P. Liu, F. Xie, J. Chen, J. Xu, Q. Chen, W. Xie, *CrystEngComm* **2019**, *21*, 5749.
- [46] a) X. Li, S. Zhang, L. Yang, X. Li, J. Chen, C. Huang, New J. Chem.
   2017, 41, 15260; b) J. Du, Y. Gao, H. Luo, L. Kang, Z. Zhang, Z. Chen, C. Cao, Sol. Energy Mater. Sol. Cells 2011, 95, 469.
- [47] T. Huang, T. Kang, Y. Li, J. Li, L. Deng, L. Bi, Opt. Mater. Express 2018, 8, 2300.
- [48] Y. Yang, B. Hong, H. Huang, Z. Luo, C. Gao, C. Kang, X. Li, J. Mater. Sci.: Mater. Electron. 2017, 29, 2561.
- [49] Y. Cao, T. Wang, N. Sepúlveda, J. Mater. Chem. C 2023, 11, 1278.
- [50] J. Ordonez-Miranda, Y. Ezzahri, K. Joulain, J. Drevillon, J. J. Alvarado-Gil, Phys. Rev. B 2018, 98, 075144.
- [51] A M. Makarevich, A G. Sobol, I I. Sadykov, D I. Sharovarov, V A. Amelichev, D M. Tsymbarenko, O V. Boytsova, A R. Kaul, J. Alloys Compd. 2021, 853, 157214.
- [52] a) K. Appavoo, D. Y. Lei, Y. Sonnefraud, B. Wang, S T. Pantelides, S A. Maier, R F. Haglund Jr., *Nano Lett.* 2012, *12*, 780; b) N. Shen, S. Chen, W. Wang, R. Shi, P. Chen, D. Kong, Y. Liang, A. Amini, J. Wang, C. Cheng, J. Mater. Chem. A 2019, *7*, 4516.
- [53] Y. Jung, H. Han, A. Sharma, J. Jeong, S S. P. Parkin, J K. S. Poon, ACS Photonics 2022, 9, 217.
- [54] N. Manca, T. Kanki, F. Endo, E. Ragucci, L. Pellegrino, D. Marré, ACS Appl. Electron. Mater. 2020, 3, 211.

- [55] H. Kim, K. Cheung, R C. Y. Auyeung, D E. Wilson, K M. Charipar, A. Piqué, N A. Charipar, *Sci. Rep.* **2019**, *9*, 11329.
- [56] a) C. N. Berglund, IEEE Trans. Electron. Dev. 1969, 16, 432; b) J. Duchene, M. Terraillon, P. Pailly, G. Adam, Appl. Phys. Lett. 1971, 19, 115; c) B. Fisher, J. Phys. C: Solid State Phys. 1975, 8, 2072.
- [57] H.-T. Kim, B.-G. Chae, D.-H. Youn, G. Kim, K.-Y. Kang, S.-J. Lee, K. Kim, Y.-S. Lim, *Appl. Phys. Lett.* **2005**, *86*, 242101.
- [58] D. Gu, H. Qin, X. Zhou, S. Xu, Y. Jiang, AIP Adv. 2018, 8, 015317.
- [59] X.-N. Sun, Z.-M. Qu, Q.-G. Wang, Y. Yuan, Acta Phys. Sin. 2020, 69, 247201.
- [60] Y. Tsuji, T. Kanki, Y. Murakami, H. Tanaka, Appl. Phys. Express 2019, 12, 025003.
- [61] Y. Zhou, X. Chen, C. Ko, Z. Yang, C. Mouli, S. Ramanathan, IEEE Electron Device Lett. 2013, 34, 220.
- [62] D. Matsunami, A. Fujita, Appl. Phys. Lett. 2015, 106, 042901.
- [63] T. Sasaki, H. Ueda, T. Kanki, H. Tanaka, Sci. Rep. 2015, 5, 17080.
- [64] S. Kabir, S. Nirantar, M. Monshipouri, M. X. Low, S. Walia, S. Sriram, M. Bhaskaran, Adv. Electron. Mater. 2021, 8, 2100428.
- [65] R. Hao, Y. Li, F. Liu, Y. Sun, J. Tang, P. Chen, W. Jiang, Z. Wu, T. Xu, B. Fang, *Infrared Phys. Technol.* **2016**, *75*, 82.
- [66] K. Abbas, J. Hwang, G. Bae, H. Choi, D. J. Kang, ACS Appl. Mater. Interfaces 2017, 9, 13571.
- [67] T. Yajima, A. Toriumi, Adv. Electron. Mater. 2021, 8, 2100842.
- [68] Y. Chen, Z. Wang, S. Chen, H. Ren, B. Li, W. Yan, G. Zhang, J. Jiang, C. Zou, *Nano Energy* **2018**, *51*, 300.
- [69] S. Chen, Z. Wang, H. Ren, Y. Chen, W. Yan, C. Wang, B. Li, J. Jiang, C. Zou, Sci. Adv. 2019, 5, eaav6815.
- [70] Y. Sharma, J. Balachandran, C. Sohn, J T. Krogel, P. Ganesh, L. Collins, A V. Ievlev, Q. Li, X. Gao, N. Balke, O S. Ovchinnikova, S V. Kalinin, O. Heinonen, Ho N Lee, ACS Nano 2018, 12, 7159.
- [71] Y. Shi, L.-Q. Chen, Phys. Rev. Mater. 2018, 2, 053803.
- [72] P.-F. Wang, Q. Hu, T. Zheng, Yu Liu, X. Xu, J.-L. Sun, Crystals 2020, 10, 764.
- [73] F. Bayram, D. Gajula, D. Khan, B. Uppalapati, S. Azad, G. Koley, Opt. Express 2021, 29, 32124.
- [74] W. Zhang, X. Wu, W. Wang, K. Zhang, B. Li, Y. Chen, ACS Appl. Electron. Mater. 2022, 4, 2101.
- [75] X.-N. Sun, Z.-M. Qu, Q.-G. Wang, Y. Yuan, S.-H. Liu, Acta Phys. Sin. 2019, 68, 107201.
- [76] S. Rathi, J.-H. Park, In-Y Lee, J. M. Baik, K. S. Yi, G.-H. Kim, J. Phys. D: Appl. Phys. 2014, 47, 295101.
- [77] A. L. Pergament, P. P. Boriskov, A. A. Velichko, N. A. Kuldin, J. Phys. Chem. Solids 2010, 71, 874.
- [78] C. Ko, S. Ramanathan, Appl. Phys. Lett. 2008, 93, 252101.
- [79] L. Fan, Y. Zhu, S. Zhao, Z. Wang, Z. Liu, L. Zhu, B. Wang, Q. Zhang, Sol. Energy Mater. Sol. Cells 2020, 212, 110562.
- [80] Y. Xiong, Qi-Ye Wen, Z. Chen, W. Tian, T.-L. Wen, Yu-L Jing, Q.-H. Yang, H-Wu Zhang, J. Phys. D: Appl. Phys. 2014, 47, 455304.
- [81] W. Xue, G. Liu, Z. Zhong, Y. Dai, J. Shang, Y. Liu, H. Yang, X. Yi, H. Tan, L. Pan, S. Gao, J. Ding, X.-H. Xu, R.-W. Li, *Adv. Mater.* **2017**, *29*, 1702162.
- [82] a) B A. Kruger, A. Joushaghani, J K. S. Poon, *Opt. Express* **2012**, *20*, 23598; b) A. Joushaghani, B A. Kruger, S. Paradis, D. Alain, J. Stewart Aitchison, J K. S. Poon, *Appl. Phys. Lett.* **2013**, *102*, 061101; c) P. Markov, K. Appavoo, R F. Haglund, S M. Weiss, *Opt. Express* **2015**, *23*, 6878.
- [83] W. R. Roach, I. Balberg, Solid State Commun. 1971, 9, 551.
- [84] A. Cavalleri, Cs. Tóth, C. W. Siders, J. A. Squier, F. Ráksi, P. Forget, J. C. Kieffer, *Phys. Rev. Lett.* 2001, *87*, 237401.
- [85] Z.-H. Zhai, Si-C Chen, L.-H. Du, S.-C. Zhong, W. Huang, Ze-R Li, H. Schneider, Q. Shi, Li-G Zhu, *Opt. Express* 2018, *26*, 28051.
- [86] Z. Wang, X. Ji, N. Dong, C. Chen, Z. Yan, X. Cao, J. Wang, Opt. Express 2022, 30, 47421.

ADVANCED SCIENCE NEWS



- [87] N. Kumar, A. Rúa, J. Aldama, K. Echeverría, F E. Fernández, S. Lysenko, Opt. Express 2018, 26, 13773.
- [88] S E. Madaras, J A. Creeden, D J. Lahneman, A. Harbick, D B. Beringer, M. M Qazilbash, I. Novikova, R A. Lukaszew, *Opt. Mater. Express* 2020, *10*, 1393.
- [89] I A. Mogunov, S. Lysenko, A E. Fedianin, F E. Fernández, A. Rúa, A J. Kent, A V. Akimov, A M. Kalashnikova, *Nat. Commun.* 2020, 11, 1690.
- [90] A J. Sternbach, F L. Ruta, Y. Shi, T. Slusar, J. Schalch, G. Duan, A S. Mcleod, X. Zhang, M. Liu, A J. Millis, H.-T. Kim, L.-Q. Chen, R D. Averitt, D. N. Basov, *Nano Lett.* **2021**, *21*, 9052.
- [91] L. Li-Bin, Lu Tie-Cheng, Lu Yong, L. Qiang, Nucl. Instrum. Meth. B 2002, 191, 102.
- [92] A. V. Scherbakov, A. V. Akimov, V. G. Golubev, A. A. Kaplyanskii, D. A. Kurdyukov, A. A. Meluchev, A. B. Pevtsov, *Phys. E* 2003, 17, 429.
- [93] H. Liu, O. Vasquez, V. R. Santiago, L. Diaz, F. E. Fernandez, J. Electron. Mater. 2004, 33, 1171.
- [94] H. Liu, S. Lysenko, A. Rua, V. Vikhnin, G. Zhang, O. Vasquez, F. E. Fernandez, J. Lumin. 2006, 119, 404.
- [95] Y. Zhang, S. Qiao, L. Sun, Qi Wu Shi, W. Huang, L. Li, Z. Yang, Opt. Express 2014, 22, 11070.
- [96] L. Wang, Z. Shao, Q. Li, J. Liu, C. Yang, P. Jin, X. Cao, Adv. Mater. Interfaces 2022, 9, 2200864.
- [97] H. Ren, S. Chen, Y. Chen, Z. Luo, J. Zhou, X. Zheng, L. Wang, B. Li, C. Zou, Phys. Status Solidi (RRL) Rapid Res. Lett. 2018, 12, 1700320.
- [98] J. Sang, P. Wang, Y. Meng, X. Xu, J.-L. Sun, Y. Wang, Z. Hua, T. Zheng, Z. Liu, C. Wang, B. Wu, X. Chen, *Jpn. J. Appl. Phys.* **2019**, *58*, 050917.
- [99] Z. Tian, B. Xu, Bo Hsu, L. Stan, Z. Yang, Y. Mei, *Nano Lett.* 2018, 18, 3017.
- [100] A. D'elia, S. J. Rezvani, A. Cossaro, M. Stredansky, C. Grazioli, B. W. Li, C. W. Zou, M. Coreno, A. Marcelli, J. Supercond. Novel Magn. 2020, 33, 2383.
- [101] Z. Yu, Y. Liu, Z. Zhang, M. Cheng, Z. Zou, Z. Lu, D. Wang, J. Shi, R. Xiong, Ceram. Int. 2020, 46, 12393.
- [102] H.-W. Chen, C.-I. Li, C.-H. Ma, Y.-H. Chu, H.-L. Liu, Phys. Chem. Chem. Phys. 2021, 23, 8908.
- [103] Z. Zhang, X. Zhao, J. Zhang, G. Bai, H. Guo, W. Liu, B. Zhang, J. Wang, L. Ji, Fu-R Chen, L. Zhao, X. Zhang, *Adv. Funct. Mater.* **2022**, 33, 2210325.
- [104] T. Tang, J. Li, Y. Mao, B. Liu, S. Peng, B. Yu, X. Liang, L. Luo, Y. Tang, K. He, Phys. Status Solidi 2022, 259, 2100596.
- [105] a) W. Rüdorff, G. Walter, J. Stadler, Zeitschrift. Für Anorganische und allgemeine Chem. 1958, 297, 1; b) A. Akroune, A. Casalot, J. Solid State Chem. 1987, 68, 163.
- [106] X. Zhou, Y. Cui, Y. Shang, H. Li, J. Wang, Ye Meng, X. Xu, Y. Jiang, N. Chen, J. Chen, J. Phys. Chem. C 2023, 127, 2639.
- [107] H. Takami, T. Kanki, S. Ueda, K. Kobayashi, H. Tanaka, *Phys. Rev. B* 2012, 85, 205111.
- [108] C.-L. Xu, L. Ma, X. Liu, W.-Y. Qiu, Z.-X. Su, Mater. Res. Bull. 2004, 39, 881.
- [109] a) A V. Ivanov, A Yu. Tatarenko, A A. Gorodetsky, O N. Makarevich, M. Navarro-Cía, A M. Makarevich, A R. Kaul, A A. Eliseev, O V. Boytsova, ACS Appl. Nano Mater. 2021, 4, 10592; b) Q. Chang, D. Wang, Z. Zhao, C. Ling, C. Wang, H. Jin, J. Li, ACS Appl. Nano Mater. 2021, 4, 6778; c) M. Li, S. Magdassi, Y. Gao, Yi Long, Small 2017, 13, 1701147; d) A V. Ivanov, O N. Makarevich, O V. Boytsova, D M. Tsymbarenko, A A. Eliseev, V A. Amelichev, A M. Makarevich, Ceram. Int. 2020, 46, 19919.
- [110] a) Y. Gao, C. Cao, L. Dai, H. Luo, M. Kanehira, Y. Ding, Z. L. Wang, *Energy Environ. Sci.* **2012**, *5*, 8708; b) S. Liang, Q. Shi, H. Zhu, Bo Peng, W. Huang, ACS Omega **2016**, *1*, 1139.
- [111] a) W. Yu, S. Li, C. Huang, RSC Adv. 2016, 6, 7113; b) C. Wu, F. Feng,
   J. Feng, J. Dai, J. Yang, Yi Xie, J. Phys. Chem. C 2010, 115, 791.

- [112] Y. Hu, Q. Shi, W. Huang, H. Zhu, F. Yue, Y. Xiao, S. Liang, T. Lu, J. Sol-Gel Sci. Technol. 2015, 78, 19.
- [113] N. Arjun, T C.-K. Yang, G.-T. Pan, Y.-L. Yang, A. Kareiva, J. Taiwan Inst. Chem. Eng. 2016, 69, 151.
- [114] K. D. Ufert, Phys. Status Solidi (A) 1977, 42, 187.
- [115] P. Jin, S. Nakao, S. Tanemura, *Thin Solid Films* **1998**, *324*, 151.
- [116] a) T. D. Manning, I. P. Parkin, C. Blackman, U. Qureshi, J. Mater. Chem. 2005, 15, 4560; b) T. D. Manning, I. P. Parkin, J. Mater. Chem. 2004, 14, 2554.
- [117] a) N. H. Azhan, K. Su, K. Okimura, J. Sakai, J. Appl. Phys. 2015, 117, 185307; b) J. Wu, L. Tong, H. Wang, G. Liu, X. Fu, T. Fan, J. Appl. Phys. 2022, 131, 85101.
- [118] a) A. Paone, R. Sanjines, P. Jeanneret, H J. Whitlow, E. Guibert, G. Guibert, F. Bussy, J.-L. Scartezzini, A. Schüler, J. Alloys Compd. 2015, 621, 206; b) M. Gurvitch, J. Vac. Sci. Technol., A 1984, 2, 1550.
- [119] S-En Chen, H.-H. Lu, S. Brahma, J.-L. Huang, *Thin Solid Films* 2017, 644, 52.
- [120] S. Taylor, L. Long, L. Wang, Thin Solid Films 2019, 682, 29.
- [121] Bo Chen, D. Yang, P A. Charpentier, M. Zeman, Sol. Energy Mater. Sol. Cells 2009, 93, 1550.
- [122] T. Hajlaoui, N. Émond, C. Quirouette, B. Le Drogoff, J. Margot, M. Chaker, Scr. Mater. 2020, 177, 32.
- [123] a) X. Lv, Y. Cao, L. Yan, Y. Li, Y. Zhang, L. Song, ACS Appl. Mater. Interfaces 2018, 10, 6601; b) C.-Y. Su, C.-C. Wang, Y.-C. Hsueh, V. Gurylev, C.-C. Kei, T.-P. Perng, Nanoscale 2015, 7, 19222; c) R M. Tromp, J B. Hannon, Surf. Rev. Lett. 2012, 09, 1565; d) H. Shin, Le T Duy, H. Seo, Ceram. Int. 2022, 48, 15748.
- [124] J. B. Macchesney, H. J. Guggenheim, J. Phys. Chem. Solids 1969, 30, 225.
- [125] M. Nygren, M. Israelsson, Mater. Res. Bull. 1969, 4, 881.
- [126] a) N. Suzuki, Y. Xue, T. Hasegawa, S. Yin, *Sol. Energy Mater. Sol. Cells* 2023, *251*, 112105; b) D. Wegkamp, M. Herzog, L. Xian, M. Gatti, P. Cudazzo, C L. Mcgahan, R E. Marvel, R F. Haglund, A. Rubio, M. Wolf, J. Stähler, *Phys. Rev. Lett.* 2014, *113*, 216401; c) G. Pan, J. Yin, K. Ji, X. Li, X. Cheng, H. Jin, J. Liu, *Sci. Rep.* 2017, *7*, 6132.
- [127] C. Wu, F. Feng, J. Feng, J. Dai, L. Peng, J. Zhao, J. Yang, C. Si, Z. Wu, Yi Xie, J. Am. Chem. Soc. 2011, 133, 13798.
- [128] S. Qin, Y. Fan, X. Qiu, G. Gou, K. Zhang, Q. Feng, G. Gan, W. Sun, ACS Appl. Electron. Mater. 2022, 4, 6067.
- [129] X. Zhou, H. Li, F. Meng, W. Mao, J. Wang, Y. Jiang, K. Fukutani, M. Wilde, B. Fugetsu, I. Sakata, N. Chen, J. Chen, J. Phys. Chem. Lett. 2022, 13, 8078.
- [130] a) D. Zomaya, W. Z. Xu, B. Grohe, S. Mittler, P. A. Charpentier, Sol. Energy Mater. Sol. Cells 2019, 200, 109900; b) J. Zou, X. Chen, L. Xiao, Mater. Res. Express 2018, 5, 065055; c) Z. Liang, Li Zhao, W. Meng, C. Zhong, S. Wei, B. Dong, Z. Xu, Li Wan, S. Wang, J. Alloys Compd. 2017, 694, 124.
- [131] J. Zhou, M. Xie, A. Cui, B. Zhou, K. Jiang, L. Shang, Z. Hu, J. Chu, ACS Appl. Mater. Interfaces 2018, 10, 30548.
- [132] J.-L. Victor, M. Gaudon, G. Salvatori, O. Toulemonde, N. Penin, A. Rougier, J. Phys. Chem. Lett. 2021, 12, 7792.
- [133] C. Batista, V. Teixeira, R M. Ribeiro, J. Nanosci. Nanotechnol. 2010, 10, 1393.
- [134] T.-L. Wu, L. Whittaker, S. Banerjee, G. Sambandamurthy, Phys. Rev. B 2011, 83.
- [135] T. Kong, M. W. Masters, S. L. Bud'ko, P. C. Canfield, APL Mater. 2015, 3, 41502.
- [136] Y. Cui, Y. Wang, B. Liu, H. Luo, Y. Gao, RSC Adv. 2016, 6, 64394.
- [137] A. Krammer, A. Magrez, W. A. Vitale, P. Mocny, P. Jeanneret, E. Guibert, H. J. Whitlow, A. M. Ionescu, A. Schüler, J. Appl. Phys. 2017, 122, 45304.
- [138] S. Guan, M. Souquet-Basiège, O. Toulemonde, D. Denux, N. Penin, M. Gaudon, A. Rougier, *Chem. Mater.* 2019, *31*, 9819.



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ADVANCED ELECTRONIC MATERIALS

## www.advelectronicmat.de

- [139] Z. Zhao, Yi Liu, Z. Yu, C. Ling, J. Li, Y. Zhao, H. Jin, ACS Appl. Energy Mater. 2020, 3, 9972.
- [140] O. Liubchenko, V. Kladko, V. Melnik, B. Romanyuk, O. Gudymenko, T. Sabov, O. Dubikovskyi, Z. Maksimenko, O. Kosulya, O. Kulbachynskyi, *Mater. Lett.* 2022, *314*, 131895.
- [141] D. Li, Z. Zhao, C. Wang, S. Deng, J. Yang, X. Wang, J. Li, Y. Zhao, H. Jin, Appl. Surf. Sci. 2022, 579, 151990.
- [142] G.-H. Liu, X.-Y. Deng, R. Wen, J. Mater. Sci. 2010, 45, 3270.
- [143] Z. Zhao, Yi Liu, D. Wang, C. Ling, Q. Chang, J. Li, Y. Zhao, H. Jin, Sol. Energy Mater. Sol. Cells 2020, 209, 110443.
- [144] R. Zhang, Bo Xiang, Y. Shen, L. Xia, L. Xu, Q. Guan, S. Tang, J. Mater. Chem. A 2021, 9, 17481.
- [145] J. Wu, Z. Wang, B. Li, B. Liu, X. Zhao, G. Tang, D. Zeng, S. Tian, *Materials* **2022**, 16, 273.
- [146] He Ma, Yu Wang, R. Lu, F. Tan, Y. Fu, G. Wang, D. Wang, K. Liu, S. Fan, K. Jiang, X. Zhang, J. Mater. Chem. C 2020, 8, 10213.
- [147] M. A. Seo, J. S. Kyoung, H. R. Park, S. M. Koo, N. K. Park, Y. S. Lim, D. S. Kim, presented at 2009 34th International Conference on Infrared, Millimeter, and Terahertz Waves, IEEE, Busan, South Korea 2009.
- [148] a) W. Zhou, M. Jiang, F. Hu, Y. Gong, L. Zhang, L. Zeng, W. Jiang, D. Li, H. Wang, W. Liu, S. Lin, X. Hou, *Appl. Opt.* 2023, 62, 1103;
  b) T. Li, H. Chen, J. Zhang, Z. Wang, *Adv. Mater. Interfaces* 2023, 10, 2202210.
- [149] a) C. Ji, Z. Wu, X. Wu, H. Feng, J. Wang, Z. Huang, H. Zhou, W. Yao, J. Gou, Y. Jiang, J. Mater. Chem. C 2018, 6, 1722; b) W. Liang, Y. Jiang, J. Guo, N. Li, W. Qiu, H. Yang, Y. Ji, S.-N. Luo, Adv. Opt. Mater. 2019, 7, 1900647.
- [150] Z. Ren, J. Xu, J. Liu, B. Li, C. Zhou, Z. Sheng, ACS Appl. Mater. Interfaces 2022, 14, 26923.
- [151] H-Fu Zhu, L.-H. Du, J. Li, Qi-Wu Shi, Bo Peng, Ze-R Li, W.-X. Huang, Li-G Zhu, Appl. Phys. Lett. 2018, 112, 081103.
- [152] F. Hu, Y. Li, X. Xu, Y. Zhou, Y. Chen, P. Zhu, S. Zhao, W. Jiang, W. Zhang, J. Han, Y. Chen, Appl. Phys. Express 2018, 11, 092004.
- [153] R-Ke Wang, H. Wang, Z.-Q. An, J.-S. He, C.-L. Zhang, G.-P. Pan, X. Li, J. Appl. Phys. 2019, 125, 163104.
- [154] H. Zhu, J. Li, L. Du, W. Huang, J. Liu, J. Zhou, Y. Chen, S. Das, Q. Shi, L. Zhu, C. Liu, Adv. Mater. Interfaces 2020, 7, 2001297.
- [155] W. Lai, R. Shi, H. Yuan, G. Liu, A. Amini, C. Cheng, ACS Appl. Electron. Mater. 2021, 3, 3044.
- [156] F. Hu, W. Guo, Qi Rong, L. Zhang, W. Zhang, J. Han, Hu Dong, Y. Zhou, J. Lightwave Technol. 2021, 39, 2476.
- [157] M. Jiang, X. Xu, F. Hu, H. Du, L. Zhang, Y. Zou, J. Lightwave Technol. 2022, 40, 156.
- [158] V. Yu. Zerov, Yu. V. Kulikov, V. N. Leonov, V. G. Malyarov, I. A. Khrebtov, I. I. Shaganov, *J Opt Technol.* **1999**, *66*, 387.
- [159] S. Kabir, S. Nirantar, L. Zhu, C. Ton-That, S. K. Jain, A. B. A. Kayani, B J. Murdoch, S. Sriram, S. Walia, M. Bhaskaran, *Appl. Mater. Today* 2020, *21*, 100833.
- [160] E. M. Guerra, D. T. Cestarolli, J. Alloys Compd. 2021, 885, 160997.
- [161] N. S. Vieira, F. A. De Souza, R. C. F. Da Rocha, D. T. Cestarolli, E. M. Guerra, Mater. Sci. Semicond. Process. 2021, 121, 105337.
- [162] A. Simo, B. Mwakikunga, B T. Sone, B. Julies, R. Madjoe, M. Maaza, Int. J. Hydrogen Energy 2014, 39, 8147.
- [163] R. Joy, Z. Han, Ke Xu, X. Pan, N. Liao, H. Zhou, Phys. Lett. A 2020, 384, 126823.
- [164] J. Huang, Yi Zhou, Y. Liu, Z. Lai, F. Zhou, J. Zhu, Mol. Phys. 2021, 119, e1900941.
- [165] Md. A Rahman, Le Cai, S. A. Tawfik, S. Tucker, A. Burton, G. Perera, M J. S. Spencer, S. Walia, S. Sriram, P. Gutruf, M. Bhaskaran, ACS Sens. 2022, 7, 82.
- [166] Ge Li, D. Xie, Z. Zhang, Q. Zhou, H. Zhong, H. Ni, J. Wang, Er-J Guo, M. He, C. Wang, G. Yang, K. Jin, C. Ge, *Adv. Funct. Mater.* **2022**, *32*, 2203074.

- [167] T. Huang, M. Qiu, P. Xu, W. Yang, L. Zhang, Y. Shao, Z. Chen, X. Chen, N. Dai, J. Mater. Chem. C 2023, 11, 513.
- [168] K. Kato, P. K. Song, H. Odaka, Y. Shigesato, Jpn. J. Appl. Phys. 2003, 42, 6523.
- [169] a) S. Dou, W. Zhang, Y. Wang, Y. Tian, Yi Wang, X. Zhang, L. Zhang, L. Wang, J. Zhao, Y. Li, *Mater. Chem. Phys.* 2018, *215*, 91; b) Y. Cheng, X. Zhang, C. Fang, J. Chen, J. Su, Z. Wang, G. Sun, D. Liu, *Ceram. Int.* 2018, *44*, 20084; c) N. Shen, S. Chen, R. Shi, S. Niu, A. Amini, C. Cheng, *ACS Appl. Electron. Mater.* 2021, *3*, 3648; d) H. Ji, D. Liu, H. Cheng, *Mater. Sci. Semicond. Process.* 2020, *119*, 105141; e) L. Calvi, L. Leufkens, C P. K. Yeung, R. Habets, D. Mann, K. Elen, An Hardy, M K. Van Bael, P. Buskens, *Sol. Energy Mater. Sol. Cells* 2021, *224*, 110977.
- [170] a) H. Han, Y. Cheng, C. Fang, J. Chen, J. Zhao, Y. Zhang, X. Zhang, J.
   *Mater. Res. Technol.* **2022**, *17*, 2026; b) H. Guo, Y. G. Wang, A. Jain,
   H. R. Fu, F. G. Chen, J. Alloys Compd. **2021**, *878*, 160352.
- [171] a) H-Na Kim, S. Yang, Adv. Funct. Mater. 2019, 30, 1902597; b) T. Moot, C. Palin, S. Mitran, J F. Cahoon, R. Lopez, Adv. Opt. Mater. 2015, 4, 578; c) S. Kabir, D. Yang, A. B. Ahmad Kayani, H. Zhang, S. Nirantar, S. Sriram, S. Walia, M. Bhaskaran, ACS Appl. Nano Mater. 2022, 5, 10280.
- [172] J. Faucheu, E. Bourgeat-Lami, V. Prevot, Adv. Eng. Mater. 2018, 21, 1800438.
- [173] L. Kang, Y. Gao, H. Luo, ACS Appl. Mater. Interfaces 2009, 1, 2211.
- [174] a) Y. Xu, W. Huang, Q. Shi, Y. Zhang, J. Wu, L. Song, *Mater. Res. Bull.* **2013**, 48, 4146; b) S. Ding, Z. Liu, D. Li, W. Zhao, Y. Wang, D. Wan,
   F. Huang, ACS Appl. Mater. Interfaces **2013**, 5, 1630.
- [175] X. Cao, N. Wang, J. Y. Law, S. C. J. Loo, S. Magdassi, Yi Long, *Lang-muir* 2014, *30*, 1710.
- [176] N. Wang, Y. K. Peh, S. Magdassi, Yi Long, J. Colloid Interface Sci. 2018, 512, 529.
- [177] R. Lopez, T. E. Haynes, L. A. Boatner, L. C. Feldman, R. F. Haglund, Opt. Lett. 2002, 27, 1327.
- [178] J. Liang, S. Wang, D. Lei, Z. Wang, X. Li, Opt. Mater. 2021, 121, 111485.
- [179] a) X. Zhao, J. Sun, J. Ma, T. Liu, Z. Guo, Z. Yang, W. Yao, X. Jiang, *Sustain. Mater. Technol.* 2022, *32*, e00420; b) X. P. Zhao, S. A. Mofid, T. Gao, G. Tan, B. P. Jelle, X. B. Yin, R. G. Yang, *Mater. Today Phys.* 2020, *13*, 100205; c) Y. Lu, X. Xiao, Z. Cao, Y. Zhan, H. Cheng, G. Xu, *Appl. Surf. Sci.* 2017, *425*, 233.
- [180] a) Y. Feng, W. Ma, H. Li, M. Yang, Y. Yu, S. Liu, X. Zeng, F. Huang,
   Y. Yang, Z. Li, ACS Appl. Mater. Interfaces 2023, 15, 5836; b) Q. He,
   Y. Wang, Y. Zhou, M. He, R. Xu, S. Hu, W. Wu, R. Wang, Opt. Mater.
   2019, 97, 109367.
- [181] Y. Gao, S. Wang, H. Luo, L. Dai, C. Cao, Y. Liu, Z. Chen, M. Kanehira, *Energy Environ. Sci.* 2012, 5, 6104.
- [182] T. D. Vu, H. Xie, S. Wang, J. Hu, X. Zeng, Yi Long, Mater. Today Energy 2022, 26, 100978.
- [183] a) S. Long, X. Cao, N. Li, Y. Xin, G. Sun, T. Chang, S. Bao, P. Jin, *Sol. Energy Mater. Sol. Cells* 2019, *189*, 138; b) M. Klinger, L. P. Tolbod, K V. Gothelf, P R. Ogilby, ACS Appl. Mater. Interfaces 2009, *1*, 661.
- [184] Z. Li, C. Cao, M. Li, L. Wang, D. Zhu, F. Xu, A. Huang, P. Jin, L. Yu, X. Cao, ACS Appl. Mater. Interfaces 2023, 15, 9401.
- [185] M. K. Shahzad, R. Z. Abbas Manj, G. Abbas, R. A. Laghari, S. S. Akhtar, M. A. Khan, M. B. Tahir, S. Znaidia, M. Alzaid, *RSC Adv.* 2022, *12*, 30985.
- [186] H. Jia, X. Ji, Z. Shao, Z. Li, A. Huang, Z. Wen, S. Gu, P. Jin, X. Cao, *Adv. Opt. Mater.* **2022**, *10*, 2200106.
- [187] S. J. Lee, S. H. Lee, H. W. Kang, S. Nahm, B. H. Kim, H. Kim, S Ho Han, Chem. Eng. J. 2021, 416, 129028.
- [188] a) Y. Ke, C. Zhou, Y. Zhou, S. Wang, S. H. Chan, Yi Long, *Adv. Funct. Mater.* 2018, 28, 1800113; b) L. Yao, Z. Qu, Z. Pang, J. Li, S. Tang, J.
   He, L. Feng, *Small* 2018, 14, e1801661; c) Y. Ke, Q. Zhang, T. Wang,

## www.advelectronicmat.de

S. Wang, Na Li, G. Lin, X. Liu, Z. Dai, J. Yan, J. Yin, S. Magdassi, D. Zhao, Yi Long, *Nano Energy* **2020**, *73*, 104785.

- [189] A. Dasgupta, A. Verma, Y. S. Chauhan, IEEE Trans. Electron Devices 2019, 66, 169.
- [190] M. Yamamoto, R. Nouchi, T. Kanki, S. Nakaharai, A N. Hattori, K. Watanabe, T. Taniguchi, Y. Wakayama, K. Ueno, H. Tanaka, ACS Appl. Mater. Interfaces 2019, 11, 36871.
- [191] a) L. Yang, K. Majumdar, H. Liu, Y. Du, H. Wu, M. Hatzistergos, P. Y. Hung, R. Tieckelmann, W. Tsai, C. Hobbs, P D. Ye, *Nano Lett.* 2014, 14, 6275; b) D. Kiriya, M. Tosun, P. Zhao, J. S. Kang, A. Javey, *J. Am. Chem. Soc.* 2014, 136, 7853.
- [192] Y. Jung, J. Jeong, Z. Qu, B. Cui, A. Khanda, S S. P. Parkin, J K. S. Poon, *Adv. Electron. Mater.* **2021**, *7*, 2001142.
- [193] a) N. Manca, T. Kanki, F. Endo, D. Marré, L. Pellegrino, *Nano Lett.* 2020, *20*, 7251; b) K. Liu, C. Cheng, Z. Cheng, K. Wang, R. Ramesh, J. Wu, *Nano Lett.* 2012, *12*, 6302; c) H. Guo, K. Chen, Y. Oh, K. Wang, C. Dejoie, S. A. Syed Asif, O. L. Warren, Z. W. Shan, J. Wu, A. M. Minor, *Nano Lett.* 2011, *11*, 3207.
- [194] a) K. Wang, C. Cheng, E. Cardona, J. Guan, K. Liu, J. Wu, ACS Nano 2013, 7, 2266; b) He Ma, J. Hou, X. Wang, J. Zhang, Z. Yuan, L. Xiao, Y. Wei, S. Fan, K. Jiang, K. Liu, Nano Lett. 2017, 17, 421.



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