Low-dimensional vanadium dioxide nanomaterials: fabrication, properties and applications

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Abstract
Vanadium dioxide (VO$_2$) receives a great deal of attention because of its intriguing properties of metal-insulator transition and its wide applications in electronics, optoelectronics, smart coatings, and so on. To further enhance the performance of their applications, low dimensional VO$_2$ nanomaterials, such as nanobeams and nanomembranes, have become a research hotspot due to their structural advantages, including large specific surface area, convenient miniaturization, light weight, and softness. In this paper, the recent studies of low dimensional VO$_2$ nanomaterials are discussed, focusing on their preparation methods, properties, and applications, as well as the existing challenges and future perspectives.

1. Introduction

Since the field of nanotechnology has evolved tremendously, low dimensional materials that refer to the bulk material whose one or more dimensions are reduced to nanoscale have developed rapidly [1]. Once the dimension decreases to nanoscale, the material properties such as optical transmittance, mechanical deformation, lattice structure, electrical transport will have novel change [2]. VO$_2$ attracts numerous research interests in the aspects of strongly correlated oxide, semiconductor, transition metal oxide and phase transition materials since VO$_2$ exhibits an extremely fast first-order metal-insulator transition (MIT) near a room temperature of ~68 °C, as demonstrated in 1959 [3]. And for low dimensional VO$_2$, it is more convenient to control the temperature artificially by stress, doping and geometrical structured design. During the MIT, VO$_2$ undergoes a lattice change from the metallic rutile R phase (high-temperature) to insulating monoclinic M$_1$ phase (low-temperature) accompanied by some noticeable properties [4]. For example, the resistivity can decrease 3–5 orders and the lattice will shrink ~1% along the c-axis when VO$_2$ changes to the metal phase which is beneficial for two-terminal electronic switch [5, 6], transistor [7], oscillator [8], thermal rectifier [9], micro-electromechanical system [10, 11], photoelectrical element [12] and metamaterial [13–17]. It is worth mentioning that the VO$_2$ insulator phase shows a high infrared transmittance (>80%) but the metal phase is almost opaque in IR region (<20%) which makes it suitable for smart window [18–20] and camouflage device [21]. With deeper research on the mechanism behind the phase transition, more potential of application of VO$_2$ has been exploring gradually.

Advanced technology needs to directly converse the external stimuli to the signals that can be the forms of micro- or nano-mechanical motion, current or voltage change, etc. Thus, among these various applications based on the distinct properties of VO$_2$, it is extensively studied in microsensors and actuators. For the development of the actuator, traditional materials including piezoelectric ceramics and shape memory alloys can only output a small displacement that cannot adapt to current development [22–27]. Although huge size change can be produced by actuator based on polymers, the second-order response time limits their application [28–33]. With emerging research on VO$_2$, it finds that its intrinsic fast MIT response (femtosecond) [34, 35] and large lattice deformation (micrometer and even millimeter) [36] make it suitable for the smart actuator which can be triggered by global heat, Joule heat and light. In addition, the VO$_2$ can be
Figure 1. The most common preparation methods for sensors and actuators based on VO₂. (a) Vapor transport for one-dimensional nanobeam [37]. (b) Pulsed laser deposition for micrometer-scale actuator [37]. Sputtering for micrometer-scale actuator (c) and millimeter-scale actuator (d) [36].

fabricated into a complicated 3D structure to satisfy all kinds of situations such as cantilever [37–45], microtube [46], nanocoil [47], micropalm [48], micromuscle [49]. Apart from actuators, diverse sensors such as H₂ [50, 51], CH₄ [52, 53], He [54], temperature [55, 56] and strain sensors [57, 58] based on VO₂ one dimensional nanowire have attracted wide attention. Typical chemical gas sensors based on metal oxide semiconductors such as zinc oxide [59, 60], tin oxide [60–67], tungsten oxide [68–70] usually need to operate at high temperature environment greater than 100 °C even about 200 °C. As such, single crystal VO₂, with the advantage of lower phase transition temperature and narrower MIT width, can break the limitation, working at low temperature while keeping high sensitivity. Moreover, combining VO₂ with catalytic nanoparticles such as Pd can not only accelerate the detection process but also enlarge the area interacting with environmental gases to raise the efficiency of sensing [50, 53, 71].

These extraordinary performances mentioned above rely on the internal properties like continuity, crystallinity, grain size, micromorphology, stoichiometry, doping, stress and so on. Thus, the preparation of VO₂ becomes a critical step which will affect the quality of devices. There are lots of fabrication methods like chemical vapor deposition [72–75], sol-gel [76–80], hydrothermal [81–83], vapor transport [84–86], sputtering [87–90], pulsed laser deposition [91–95], atomic layer deposition [96, 97], etc. According to different situations of devices, we should choose the suitable chemical or physical fabrication methods. Although many reviews on synthesis of VO₂ film or particle have been reported recently [98–101], which methods can be applied to actuator and sensor has rarely been summarized. This review mainly focuses on some classical VO₂ preparation methods towards actuator and sensor as illustrated in figure 1. From the bottom, VO₂ basic phase transition behavior is outlined in section 2, covering the transition of crystal structure and electronic band structure, and the upper level in sections 3, 4 and 5 will be followed by introducing the vapor transport, pulse laser deposition and sputtering method. Then, the top level includes some interesting actuators and sensors application based on these methods. Besides, some other methods will also be discussed in section 6. Finally, we will consider the outlook for future applications of VO₂ and develop direction of synthesis methods.
2. The phase transition of VO$_2$

The mechanism of the VO$_2$ phase transition has been studied for decades. As we know, polycrystalline VO$_2$ film will have 3–4 order change of the resistance as shown in figure 2(a) [46], and for single crystal VO$_2$, the change magnitude could reach 5 orders, accompanied by a crystal lattice transition from insulator M phase (low temperature) to metal R phase (high temperature). The lattice transition schematic diagram is illustrated in figure 2(b) [102]. VO$_2$(M) is low symmetry monoclinic structure in room temperature where V–V distance along the z axis are 3.19 Å and 2.60 Å between the nearest vanadium atoms forming a zigzag atom chain [103, 104]. When the temperature rises and goes beyond VO$_2$ phase transition critical temperature (~68 $^\circ$C), the distorted rutile structure changes to tetragonal structure VO$_2$(R) where V$^{4+}$ ions occupy the corner and center positions of the lattice, and each V atom is surrounded by six O atoms forming an octahedron unit cell. The adjacent V–V distance is ~2.85 Å along the z axis chains equally [105, 106].

In 1971, Goodenough first gave a theoretical study of the VO$_2$ energy band structure, as shown in figure 2(c) [108]. The left is low temperature condition in which the V atoms of dimerize causing splitting of the d$_{14}$ band into fully occupied and the anti-bonding. Meanwhile, the $\pi^*$ orbitals move to higher energies being empty. Thus, there is an e.g. ~0.6–0.7 eV bandgap between d$_{14}$ band and $\pi^*$ band where the Fermi energy exists and now VO$_2$ performs as an insulator. While after the MIT, the VO$_2$(R) whose Fermi energy state falls between the d$_{14}$ orbitals and anti-bonding $\pi^*$ orbitals showing the metallic characteristics [102, 109–111].

Although the electric band and MIT behavior of VO$_2$ has been investigated intensely for decades, the mechanism of MIT phase transition remains elusive. The viewpoints toward the MIT mechanism are mainly divided into two models: a lattice distortion driven (Peierls-like) transition [112–114] or an electron correlation driven (Mott-like) transition [115, 116]. And the latter theory was discussed again by Qazilbash et al [107, 117]. They used infrared spectroscopy and nano-imaging technology to detect the color of different phase regions of VO$_2$, as shown in figure 2(d). Because of the difference of optical constants, the amplitude of the scattering signal will increase in metallic regions compared with that in the insulating regions. When VO$_2$ is insulator phase below 341 K, the color shows almost all dark blue, but with the temperature increasing, some light blue clusters appear and eventually connect, indicating the process of metal region nucleate. When the temperature is high enough, almost all the regions merge together and become blue even with some white spots meaning that the insulator phase transforms to metal completely. This indicates that the metallic puddles are not simply isolated regions but a clear signature of electronic correlations. Their work may help to understand the decades-long debate from a new viewpoint. Indeed, it is difficult to make a full understanding of the MIT completely only according to one model. Many researchers hold the view that the MIT mechanism in VO$_2$ is a mixture of Mott (electronic) transition with a Peierls (lattice) lattice in terms of ‘Peierls-Mott’ transition [118].


3. Vapor transport

3.1. Fabrication of VO₂ nanobeams

Vapor transport has become a common method often used in single crystal nanobeam preparation since the 1960s [84]. The mechanism behind this process is not such complex: The condensed or powder source materials are vaporized at high temperature and the resultant vapor phases form the desired products under certain conditions (temperature, pressure, atmosphere, substrate, etc.). A schematic diagram of the apparatus often used in many experiments shown in figure 3(a) [119]. The synthesis processes are usually conducted in a quartz or alumina horizontal tube furnace and the source materials are loaded on the boat positioned at the center of the tube. The carrier gas enters at the left end and is pumped out at the right end of the tube furnace. Several plates set on the right inside the tube which act as the substrate for single crystal growth.

Park group firstly introduced the vapor transport process to synthesis VO₂ nanobeams or nanowires in 2005 [85]. They used VO₂ powder fabricating the well-faced with an approximately rectangular cross-section VO₂ nanobeams as shown in figure 3(b). The well-prepared one-dimensional nanowires were grown under temperature \( T = 900–1100 ^\circ C \), pressure \( P = 12–13 \text{Torr} \) and time \( t = 5 \text{ h} \). The most striking feature is the uniform VO₂ nanobeam, strongly suggesting that the VO₂ nanowires have a preferential growth direction. In terms of how the VO₂ single crystal can grow using vapor transport, many researchers described their viewpoints successively [86, 120–123]. Among them, Strelcov et al proposed the nucleation and growth of VO₂ firstly and most comprehensively [86]. They utilized high-quality optical microscope to monitor the nucleation and growth of VO₂ in situ, in real time, and in a wide temperature range suggesting that liquid droplets of \( \text{V}_2\text{O}_5 \) nucleate prior to VO₂ growth, and these droplets may coexist with VO₂ nanobeams at the growth front. As shown in figures 3(c) and (d) originally the precursor (a fine powder of \( \text{V}_2\text{O}_5 \)) melt and aggravated into microscopic droplets. As the temperature rose, the new phase (VO₂) created at the developing apex of the nanobeams with the feeding materials supplied via the peripheral liquid wetting layer (\( \text{V}_2\text{O}_5 \)). The excessive deposition time enables the abundant supply of reacting molecules and extended chemical reaction. Then the crystalline nuclei grow inside the droplet along the direction perpendicular to the facet of minimal surface energy. These newly formed crystalline nanowires grow at the expense of the surrounding host liquid. When the nanostructure growth out of the host droplet, a material delivery channel forms for the nanowire growing front. Droplets are immovable owing to strong interfacial interaction with the substrate. More importantly, the aforementioned growth scenario depends on heating rate, temperature and oxygen partial pressure because vanadium can form a variety of stable stoichiometries.

Previous synthesis of these nanostructures is limited in density, aspect ratio, single-crystallinity, or the as-grown VO₂ nanowires are embedded into the substrates with short lengths (typically less than 50 \( \mu \text{m} \)). Until 2012, Chun Cheng et al break these limitations and synthesize ultra-long, ultra-dense, and free-standing VO₂ micro/nanowires (MNWs) using a simple vapor transport method (see figure 4(a)) [120]. The growth reaction was carried out in the following condition: source: \( \text{V}_2\text{O}_5 \) powder, evaporation temperature: \(-880 ^\circ C \), Ar flow rate: \(-6.8 \text{sccm} \), pressure: \(-5 \text{Torr} \), evaporation time: more than 2 h. The key to forming high density and ultra-long nanowires is the choice of substrate surface: the highest density could be achieved on a rough substrate surface, while polished quartz or other species of substrates turn out much lower densities of MNWs which are strongly embedded or clamped on the substrates. The growth mechanism of free-standing MNWs is illustrated in figure 4(c). At first, the VO₂ nucleates a \( \text{V}_2\text{O}_5 \) droplet and stick onto the local substrate surface plane owing to the capillary forces. After a while, initial VO₂ MNWs grow along the surface roughness. After the growth front grows out the plane, the MNWs become
free-standing. In addition, compared to MNWs grown embedded in substrates, the free-standing MNWs can expose more surface to the gas reactant allowing more reactant molecules being adsorbed and diffusing to the growth tip. Therefore, it will result in a faster free-standing growth and longer axial length. The longest VO$_2$ nanowire could reach 5 mm as shown in figure 4(b). The XRD shows a representative spectrum of MNWs and demonstrates clearly that the produced MNWs are crystalline (figure 4(d)). Figure 4(e) shows the resistance versus temperature of four devices that were cut from one single MNW. These four devices show the same resistance behavior of changing four orders during the MIT. The difference in MIT temperature and hysteresis width between devices is probably caused by the axial stress state.

3.2. Applications of VO$_2$ nanobeams

As the VO$_2$ single crystal fabrication technology matures, a number of researches based on it have been performed owing to the unique properties of single crystal. For example, Wu group studied the domain structure and phase transition of VO$_2$ induced by external stress [124–126], because the free-standing, single-crystal nanostructures are dislocation-free and can be subjected to coherent and continuously tunable external stress. When they established coherent strain fields in the VO$_2$ beams by bending or applying uniaxial stress, the periodic, micro-scale phase domains could be distinguished under optical microscopy. Beside of controlling the phase transition by stress, they also achieved by graded doping [122]. This provides new opportunities for controlling the phase domain and internal stress. As we all know that substitution of V$^{4+}$ with W$^{6+}$ can lower the MIT temperature. When the quantity of W varies continuously along the nanowire axis, the phase transition with the raising of temperature will be gradual instead of abrupt, achieving arbitrary regulated MIT temperature. Such a device may open the wide application in thermal/mechanical sensing. To date, most of the works have been focused on studying the gas sensing. Strelcov et al studied the MIT behavior of single crystal VO$_2$ nanobeam under different pressure [54]. The schematic diagram of the device is illustrated in figure 5(a). Because the MIT was triggered by the competition between accumulated Joule heat and the heat dissipating to ambient gas, various gas pressure would affect the thermal conduction process which was recorded by MIT voltage as shown in figure 5(b). The raising of Ar pressure which caused faster thermal loss could be accompanied by higher MIT threshold voltage. They also tried other kinds of gas and found different trends of MIT voltage versus pressure. Thus, this device is not only a gas sensor but also working as a pressure sensor being suitable for various gases. In addition, other kinds of gases are also been always explored such as H$_2$, Ar and CH$_4$. Continuous efforts have been concentrated on the improvement of sensitivity and selectivity such as decorating VO$_2$ with Au, Pt nanoparticles which can enlarge the surface area contacting with atmosphere or promote catalytic performance [50–53, 71].

Furthermore, since nanobeams can withstand a much higher uniaxial strain without plastic deformation or fracture, VO$_2$ nanowire is also a practical tool to probe the strain state besides the gas sensor. Bin Hu et al prepared nanobeams with lengths ranging from tens to more than 100 µm [57]. And they made them lift down transferring to the polystyrene substrate by silver paste and fabricated into a device shown in figure 5(c). They probe the room temperature M$_1$–M$_2$ phase evolution in a single end-clamped VO$_2$ nanobeam subjected to tensile and compressive stress. Previous works have proved the stabilization of the M$_2$ phase by applying uniaxial compressive strain in the [110] direction in pure VO$_2$. Thus, as shown in figure 5(d), with the uniaxial tensile strain along the c$_R$ direction, the fraction of the M$_2$ phase increased in order to release the strain in the nanobeam. And the relatively high electrical resistance of the M$_2$ phase compared to the M$_1$
Figure 5. (a) Schematic diagram of the working principle of gas sensor based on VO$_2$ nanobeams. (b) I–V scan of VO$_2$ nanobeam under different Ar pressure [54]. (c) Strain sensor device on the left and optical image of bonded nanobeam on the right. (d) Schematic of the phase transition of M$_1$ and M$_2$ with tensile and compressive strain. (e) The I–V curve under different tensile and compressive strains [57].

phase also induced the decrease of the conductivity correspondingly. In contrast, compressive strain can release the preloaded strain in the nanobeam and decreases the fraction of the M$_2$ phase and thus increases the conductivity. Loading the tensile or compressive strain bent the device step by step with very little increment (~0.05%), and we can observe that the change of the I–V behavior was strongly dependent on the loading strain as shown in figure 5(e). The I–V curves of the VO$_2$ nanobeam shifted downward with tension and upward with compression which arises from the M$_1$–M$_2$ phase transition in the nanobeam. In addition, the response time was studied and exhibited a quick response to the strain switches. Thus, this kind of flexible strain sensor based on VO$_2$ nanowire has high sensitivity, quick response time and good reproducibility at room temperature.

4. Pulsed laser deposition

4.1. Fabrication of VO$_2$ nanomembranes

Pulsed laser deposition (PLD) as a physical vapor deposition technique was first used for semiconductors and dielectric thin films in 1965 [127]. Then with the development of complex chemical stoichiometric oxide film like oxide ceramics, superconductors, dielectric materials, etc, this method came into sight gradually because of the advantages of non-thermal step, versatility, congruent (stoichiometric) transfer, accurate thickness control. And PLD enriches the oxide films research filed in turn.

The biggest characteristic of PLD is stoichiometric transfer which means the elemental ratios of film are the same with ablated target materials [93, 128]. This is determined by nature of its preparation steps: (i) High energy laser focus on the target and the electromagnetic energy is immediately converted into electronic excitation forming an extremely dense plasmon including atoms, molecules, most ions and of course electrons but overall being electrically neutral. The KrF laser is a regularly used kind and usually with the fluence of 1–5 J cm$^{-2}$. And the produced plasma ions have high kinetic energies ranging more than 100 eV and the mean energy of the atoms is much lower, on the order of 5–10 eV [129]. The kinetic energies of the ablated species lie mainly in a range that promotes surface mobility while avoiding bulk displacements which will rarely decompose or destroy the material [130]. This fast and strong heating (up to 5000 K inside the plasma) within nanoseconds far from thermal equilibrium which ensures that material components evaporate at the same time as a ‘package’ [128]. So, the stoichiometric transfer can be achieved. (ii) The plume expands perpendicular to the target with an identical angular distribution and continuously absorbs the laser heat (shown in figure 6(a)). Thus, the bulk material under the plasma is largely screened from the remainder of the laser pulse and avoid being directly thermal decomposition [130]. (iii) The initial velocity of plume is about 10$^6$ cm s$^{-1}$ [93]. This process usually involves the addition of background gas such as Ar and O$_2$ which will reduce the velocity because multiple collisions between them dissipating the kinetic energy of the plume. Then it expands continuously until reaching the substrate (for example: Si wafer) and the velocity is slow enough to nucleate and form nanoclusters during every pulse. Traditional thermal
evaporation transport target material to substrate via vaporizing the bulk material under high temperature environment which can hardly preserve the stoichiometry of target material because decomposition will happen before enough vapor pressure was reached [128]. Although the sputtering method is also a kind of non-thermal method, it cannot ensure the same stoichiometry with target because working gas (for example: argon) is needed to ignite the electrical discharge which makes deviation of the sputtered component (will be introduced below) [130, 131]. Therefore, the advantages of PLD described above set it apart from other method and almost any condensed matter material can be ablated by laser. However, there are also some drawbacks. For example, although the target material under the plume is shielded from further direct ablation, it is indeed affected by the plasma heat, which leads to the ejection of macroscopic particulates called ‘laser droplets’ [128], doing harm for the film growth. Besides, angular energy distributions within the plume will limit the deposition area typically to a few cm², not suitable for large scale film preparation [132].

As PLD was popularized among film preparation, it was also developed for use with VO₂ film deposition in 1993 by Borek who used vanadium target in specific oxygen and argon ratio [91]. Figure 6(b) shows an SEM micrograph of a typical VO₂ film deposited on a sapphire substrate, showing that the grains have an irregular shape with a grain size of less than 0.5 μm. Small pinholes are also observed in the micrograph. Owing to the stoichiometric transfer of PLD, one can prepare VO₂ film by using VO₂ target directly. Maaza was the first to report room-temperature growth of VO₂ by VO₂ target with laser energy density of 0.5 ± 2.7 J cm⁻², and the as-deposited films showed rather sharp phase transitions at around 70 °C [94]. But the surface still remained rough. With the progress of fabrication methods, it has become the most popular technique for VO₂ thin film and nanoparticle fabrication in recent times. About the VO₂ growth mechanism during PLD process, Suh et al studied the nucleation and growth of VO₂ nanoparticles and thin films [133]. Vanadium oxide was prepared by pulsed laser deposition and followed by thermal oxidation to create VO₂. The vanadium oxide materials were grown on the n-type silicon substrates (~2 cm in diameter and 500 mm thickness). The beam from a KrF excimer laser (wavelength of 248 nm with 25 Hz pulse rate) was focused onto a vanadium target (~99.95% purity) at a fluence of 4 mJ cm⁻². The VO₂ films deposited by PLD would turn to nanoparticles on substrate instead of film. And mostly, the subsequent thermal oxidation process is needed to help continuous and dense film forming. Nevertheless, if the thickness is thin enough (lower than 100 nm), the nanoparticle will aggregate, leading to the formation of isolated larger clusters VO₂ as shown in figure 6(c). And the temperature of thermal oxidation is the critical parameter. When temperatures up to 450 °C, the nanoparticles are nearly hemispherical VO₂ (figure 6(c)), while above 550 °C (figure 6(d)), the hemispherical nanostructure tend to a hill indicating the V₂O₅ because of the rise of wetting. This phenomenon was confirmed by Pauli who studied the growth of VO₂ nanoparticles on silicon and sapphire [95]. Since accurate stoichiometry VO₂ film being prepared by PLD, the films are applied in microactuators field because high-quality and uniform VO₂ can produce large size deformation owing to the lattice deformation.

4.2. Applications of VO₂ nanomembranes
This preparation technique using high energy ablation and assisted with subsequent thermal annealing process can prepare high-quality VO₂ film which is suitable for micro-scale devices. In this regard, Nelson
Figure 7. (a) SEM image of SWNT/VO$_2$ film. The scale bar is 500 nm. (b) Schematic diagram of SWNT/VO$_2$ cantilever. (c) Displacement and response time of SWNT/VO$_2$ and VO$_2$ cantilever under low laser power [37]. (d) SEM cross-section image of a VO$_2$ film deposited on SiO$_2$/Si substrate. The scale bar is 500 nm. (e) The large bending amplitude of Cr/VO$_2$ bimorph during MIT. The scale bar is 50 µm. (f) Actuating the entire micropalm by laser [48]. The scale bar is 50 µm. (g) SEM cross section image of 30 nm VO$_2$ nanomembrane [134]. (h) Temperature dependence of the emittance for 1.0 at.% W doped VO$_2$-based device [135].

Group did lots of researches on VO$_2$ cantilever microactuator mostly based on this method. They created a preliminary microactuator based on VO$_2$/Si cantilever in 2009 whose length was 350 µm with 115 µm tip displacement [44]. The change in curvature of over 2000 m$^{-1}$ was calculated. Then in 2010, they elevated the change of curvature to 2500 m$^{-1}$ with length of 300 µm [40]. And by laser stimulation, the response frequencies could achieve greater than 100 Hz and even up to frequencies of a few kHz with no amplitude degradation after tens of thousands of pulses. If combining the single-wall carbon nanotubes (SWNT) with VO$_2$ [37], they prepared ~120 nm thick VO$_2$ film by PLD (used metallic vanadium target, at 595 °C, with oxygen gas pressure at 20 mTorr) and transferred 500 nm thick SWNT on it, forming SWNT/VO$_2$ cantilever (shown in figures 7(a) and (b)). It was found that larger displacement could be produced under low laser power (compared to pure VO$_2$ cantilever) as shown in figure 7(c). This is because the thicker SWNT could enhance the light absorption and correspondingly reduced the amount of photothermal energy required for actuation. Therefore, not only the bending displacement was larger than the pure VO$_2$ but also the response speed could be faster because more thermal energy leading to a more complete phase transition.

Besides classical cantilever structure, the PLD can be also applied to fabricate more complicated structure. Junqiao Wu group fabricated a giant-amplitude (~100 µm), high-work density (0.63 mJ cm$^{-3}$) VO$_2$ microactuator looking like a micropalm [48]. During the PLD, the chamber was pumped with oxygen and the pressure stabilized at 10 mtorr. The substrates were heated to 520 °C and the rate of deposition is about 2.6 nm min$^{-1}$ using VO$_2$ target. Cr layer was deposited on the VO$_2$ to form stress difference. The prepared film SEM cross-section as shown in figure 7(d). And after photolithography and etching the SiO$_2$ under the VO$_2$, a micropalm was formed. Every arm of the palm showed good response to external stimuli. Owing to the good electrical conductivity of the Cr and VO$_2$ layers, a small applied input power of 1.6 mW (voltage 1.4 V) rendered the actuator to bend (figure 7(e)). The laser can address each finger of the palm individually at room temperature with a low power of ~4 mW and can also activate the entire palm structure bend globally (figure 7(f)). Here, in order to heat the entire palm structure beyond the MIT temperature by laser, they elevated the substrate temperature to 53 °C because of the limitation of the maximum laser power. In addition to working in ambient air, the actuator also worked well in aqueous environment.

Recently, the thermochromic property of VO$_2$ nanomembrane has made it a thermal control material which is applicable for smart radiation device and spacecraft [134–140]. The transition occurs at ~68 °C accompanied by the increase of IR reflectivity and the decrease of IR emissivity as the temperature increases. However, Benkahoul group has found that the emissivity of VO$_2$/Al systems behave increasing emissivity with higher temperature, which is good for the spacecraft to maintain its temperature by adapting the radiated heat of VO$_2$. This is attributed to the high IR reflectivity of Al substrate compared to quartz or silicon [136]. Then, Hendaoui employed W doped VO$_2$/SiO$_2$/Au layered structure by PLD whose the highest emittance could reach 0.8 (figure 7(h)) [135]. And by tuning the content of W element, it could achieve a large tunability of spectral emittance in a wide range of temperature. In figure 7(g) we can also observe the island grains of 30 nm VO$_2$ nanomembrane prepared by PLD which confirms the growth mechanism described above [134].

We believe that as the development of PLD technology, the continuity and density could be further improved and achieve the arbitrary scale while the film maintain high quality. It will do much good to the integration of the present devices into larger micro-electro-mechanical system (MEMS) or micro-systems.
5. Sputtering

5.1. Fabrication of VO$_2$ nanomembranes

Sputtering holding the advantages of uniformity, high density and efficiency of deposition has been a commercially used method to prepare two-dimensional film. With the development of this technique, almost any materials can be deposited by sputtering. The film composition can be the same with target material or by reaction with background gas. Nowadays, magnetron sputtering has been the most popular method used in experiment which is the point we discuss here. The construction of sputtering includes a diode geometry and a high-vacuum chamber. Working gas (usually argon ions) is injected into the chamber which works as energetic ions to bombard a target served as a cathode and the target atoms fly towards and deposit on the substrate (the anode) facing the target, forming a coating. And a planar magnetic field is added around the target. The diagram of apparatus is shown in figure 8(d), the other gadgets remain the same but the magnetic field which will confine the electrons around the discharge region which will produce higher plasma density, more energetic ions and higher sputtering efficiency. The ion bombard process is a critical parameter which strongly influences the structure and properties of the growing film [141, 142]. The ‘heat spike’ model well described the bombardment physical process as below [131]: The kinetic energy range of the projectile particles for sputter deposition lies approximately between 100 and 1000 eV. The energy is transferred from the projectile particles sequentially to the atoms in the near-surface region of the solid material to be sputtered which is called ‘knock-on’ process [143]. And the scattering cross-section for this process is still large enough that the penetration depth is only a few tens of monolayers. However, if one enhances the energy of projectile particles over keV-range, the projectile particles will transfer its energy to the region rapidly and all the bonds of atoms around the point of impact are simultaneously broken, which will damage the deposition quality. When the energy is increased far above keV, the incident ions begin to lose enough energy and implant in the target eventually.
Compared to PLD, the most advantage of sputtering is the capability of large-scale film preparation because the sputtered area is much larger than PLD. However, there are rarely using VO$_2$ target to prepare VO$_2$ film directly. Because sputtering utilizes momentum transfer between the incident ion and the target atom surface, the average sputtered stoichiometry may deviate from the components of target such as enrichment of the heavier component in target region [131]. In the field of VO$_2$ preparation, sputtering has been used since Ful et al firstly used vanadium target to prepare VO$_2$ thin film by reactive ion sputtering [88]. The reactive sputtering was carried out with a standard DC sputtering apparatus with an ultimate pressure of $5 \times 10^{-7}$ torr. The sputtering rate for these conditions was 35 Å min$^{-1}$. The substrate was heated at 400 °C during the sputtering process and after that, it is a 30 min post-deposition annealing. The conductivity change was also taken in figure 8(a). As the temperature is increased there is a sharp transition in conductivity at approximately 345 K indicating a good crystallization. And then the DC-magnetron sputtering was firstly introduced to prepare VO$_2$ film by Kusano [145]. They also used pure vanadium target which was deposited at 400 °C using an optimized O$_2$ injection rate (slightly higher than 0.60 mTorr). A typical resistivity change could reach 3–4 magnitudes also showing great performance. Nowadays magnetic sputtering has become the most popular film preparation method because of the high efficiency, high density, large area and controllable thickness. Recently, a new sputtering called high power impulse magnetron sputtering appeared to fabricate VO$_2$ film which can produce extremely high ionization degree of the target material under high power (600–800 W), thus it can obtain much denser crystalline films compared to conventional DC-magnetron sputtering. Figures 8(b) and (c) illustrate the AFM and SEM images of VO$_2$ films prepared by Aijaz [144] and Fortier [87] in which we can see a denser grain alignment.

Even though sputtering is a kind of physical vapor deposition, it is always used to dope other elements during fabrication procedure. Actually, the doping method is extremely simple but convenient which is beneficial from the advantage of the sputtering. For most of studies, they just put the metal or alloy stripes or pieces on the vanadium target and the doping elements are bombarded and grow on the substrate along with vanadium because almost any materials can be deposited by sputtering. The doping concentration in VO$_2$ thin films can be adjusted precisely by varying the quantity of metal stripes or pieces. And a co-doping mode was invented by Wang et al as shown in figure 8(e) [146, 147]. There is more than one target in the vacuum chamber, so they could obtain pure VO$_2$ film and doped VO$_2$ film simultaneously by moving the substrate position. The doping ratio could be tuned not only by the area of doping target, but also changing the DC sputtering power of target. Until now, various elements have been studied such as W [146, 148], Cr [149], Ti [148] and Ru [150] which induce shrinkage of crystal size and local tetragonal phase. For example, with the Ti or Cr introduced, the optical transmission in visible and infrared region of VO$_2$ film (insulator phase) had been enhanced and the modulation amplitude was increased in terahertz region. And generally, lower phase transition temperature is desirable because most of the applications such as smart window, modulator and detector are applied at room temperature to show their performance.

Since the oxygen is always participating in the VO$_2$ growth as a reactive gas and temperature is also a decisive parameter for crystallization, there are many researches to optimize the condition [90]. Chain group has studied the effect of oxygen percentage and substrate temperature on the VO$_2$ film growth [151, 152]. They varied the oxygen fraction of gas pressure from 10% to 50%. The 10% oxygen samples were identified as a low-oxide mixture VO$_{0.9}$ and VO$_2$ appeared during an oxygen percentage of 15–25%. When the oxygen fraction beyond 30%, much more oxygen leads to the form of V$_2$O$_5$. Nevertheless, the ratio of V and O atoms with the varied temperature did not show the same tendency as oxygen percentage. The ratio was between 0.38–0.55 for all films but the structure showed relation with different temperatures. The films in the range of 350 °C $\leq$ T $\leq$ 435 °C appeared as poorly defined grains. The T was not likely to be high enough to encourage oxidation of the vanadium. And for the 505 °C $\leq$ T $\leq$ 570 °C, the films consisted of oriented, columnar grains with 100–200 times change of electrical conductivity which indicated the phase of VO$_2$. Eventually, the films with large and well-defined grains displayed the best optical and electrical switch at 505 °C $\leq$ T $\leq$ 570 °C. From the discussed above, we can conclude that proper sputtering condition plays a decisive role in VO$_2$ film quality. As the sputtering technique becomes mature gradually, it is also applied not only in micro-scale actuator as PLD but also in millimeter-scale actuator.

5.2. Applications of VO$_2$ nanomembranes

Sputtering is widely used in the fabrication of VO$_2$ film along with the sputtering technology become mature gradually. He Ma et al developed flexible, all-inorganic actuators based on bimorph structures composed of VO$_2$ and carbon nanotube (CNT) thin films [36]. The driving force of VO$_2$/CNT actuators originates from the MIT of VO$_2$ triggered thermally by external stimuli as illustrated in figure 9(a). They found that VO$_2$ is orientated along the (011) plane on CNT films preferentially, so the $c_b$ axis of VO$_2$ generally sits in the plane of VO$_2$/CNT films. When heated beyond the MIT temperature, VO$_2$ shrunked along the in-plane direction and VO$_2$/CNT cantilever to bend toward the VO$_2$ side. And we can see that the tip displacement could reach...
800 μm under ΔT = 18 °C (figure 9(b)). They also sputtered VO₂ on carbon nanocoils (CNC) just as shown in figure 9(c) which showed similar behavior under laser radiation like the above mentioned VO₂/CNT [47]. The large displacement of 20 μm when the temperature increased by 10 °C (figure 9(d)) demonstrated the film continuity and density prepared by sputtering. As the design of 3D structure springs up, Ziao Tian et al applied VO₂ prepared by sputtering using V₂O₅ target into smart device, fabricating free-standing 3D reconfigurable microtubes and microhelix VO₂ actuators [46, 153]. The different thickness of Cr layer induced different initial strain of Cr/VO₂ bimorphs. Figure 9(e) illustrates the process of self-rolling microtube after the stress released. The greater strain causing smaller diameter of microtube had lower MIT threshold voltage owing to compressive strain in VO₂ nanomembrane as shown in figure 9(f). It shows us a novel way to tune the MIT temperature through 3D structure. Besides, the 3D microhelix based on pure VO₂ nanomembrane was fabricated from 2D pattern successfully owing to the lattice mismatch between polycrystalline VO₂ and substrate. Figure 9(g) demonstrates that the helix local region can be triggered by 808 nm laser with a power density of 0.03 mW μm⁻² reversely. And the deformation at about 30 μm can be clearly observed under the optical microscope (figure 9(h)), showing the high quality of the film prepared by sputtering again.

As we described in 5.1, the most inviting feature of sputtering is the capability of large-scale film preparation which has been made full use by some applications. For example, an integrated smart window composed of graphene-supported VO₂ on poly(ethylene terephthalate) (PET) substrate was fabricated by Kim et al [20]. As shown in figure 10(a), a large-scale VO₂ film was sputtered on graphene covered copper substrate, then the copper was etched and the rest was transferred onto PET using roller. After these processes like high temperature, etching and transferring, the flexible but robust smart window still performed excellent energy-saving function. Besides this, a flexible millimeter-scale actuator based on CNT/VO₂ was fabricated by sputtering [36]. It could produce giant amplitude and fast response time under laser trigger because of the large light absorption of CNT shown in figures 10(b) and (c). Further, a biomimetic hand with four fingers was fabricated (figures 10(d) and (e)) base on it which was controlled to open or close by the laser irradiation. It could move a paper slip which was 30 times heavier than the hand itself. Besides, sputtering also can be an effective method to prepare thick VO₂ film. Dey et al prepared
vanadium oxide-molybdenum oxide (VO-MO) as thick as 2300 nm while the average Young’s modulus and nanohardness could reach ~135.1 GPa and ~2.14 GPa, respectively. The dense structure shown in figure 10(f) can reflect that sputtering technique offers a highly crystalline nanocolumnar structure for the VO-MO film thus it could possess such robust mechanical property. Moreover, the introduction of molybdenum oxide decreased the transition temperature to around 45 °C–50 °C and reflectance to 0.2 (figure 10(g)), combining with the original high emittance beyond the phase transition temperature, which can achieve thermal auto modulation for solar cell and smart radiation device [137].

In summary, the sputtering method not only is capable of micro-scale film fabrication, but also preparing millimeter-scale film, both with good continuity and density. And it is very convenient for doping during this sputtering process which provides new ideas for tuning the phase transition properties of VO₂ actuators.

6. Other methods

Besides the three main methods mentioned above, there are still other methods which are often used in VO₂ preparation such as sol-gel method, hydrothermal method, atomic layer deposition, chemical vapor deposition and so on.

Sol-gel method is applied for depositing VO₂ films because it has many advantages such as large area fabrication, low cost, and the feasibility of various stoichiometries and doping. This method consists of spin-coating gel precursor (usually metal alkoxides and metal chlorides) and a subsequent annealing process under specific temperature, oxygen pressure and time. But various stoichiometries also means the formation of the pure phase is not easy for the sol-gel technique due to the difficulty in controlling the annealing condition which is known to be crucial for forming the VO₂ phase. This method was firstly introduced to VO₂ preparation by Greenburg in 1983 who fabricated pure VO₂ and doped with tungsten, molybdenum or
niobium [76]. Then, the Guzman group and Livage group widely used sol-gel method using vanadium alkoxides and studied the electrical and electrochemical properties of VO$_2$ film [154–156]. In 2006, Byung Gyu Chae et al improved the sol-gel method with a more simplified annealing process which was subsequently operated in a low pressure of oxygen [157]. And they used the above-mentioned method to fabricate VO$_2$-based two-terminal devices which could be utilized as a programmable critical temperature sensor [158]. Owing to the convenience of doping during the gel synthesis, Mukherjee et al doped or co-doped various elements such as F, W, Ti, Mo. They found that different element doping could induce wider or narrower optical band gap which performed high transparency or opaque. The reversible and repeatable phase transitions at sub-zero level of temperatures $-$24–26.3 $^\circ$C and low solar absorbance make it have a wide application prospect in smart radiative device applications in spacecraft [138, 139].

Hydrothermal is similar to sol-gel method to some extents. Its process also includes precursor and annealing, but the precursor often are vanadium salt solution and oxalic acid instead of forming sol-gel. Hydrothermal product is a metastable phase or mixture phase, rather than the pure VO$_2$(M) [159]. Thus, the morphologies are various owing to different phase states such as nanorod, nanosheet, nanoflower, nanoflake, microsphere and so on. For example, Li et al synthesized VO$_2$@TiO$_2$ nanorod structure as shown in figure 11(a) which combine the modulation ability for IR light of VO$_2$ and the photocatalysis for organic dye of TiO$_2$. Because of the ‘interfacial doping’ by core–shell structure, the original IR light transmittance could be enhanced owing to the Ti element introduced (figure 11(b)) [160]. Furthermore, these structures hold high surface-to-volume ratio which makes VO$_2$ a good candidate for humidity and gas sensing. For example, Zhu Hongmei et al studied the gas sensing behavior of the flowerlike VO$_2$(B) powders toward a variety of flammable and toxic gases such as ethanol, acetone, butanol and isopropanol [161]. Aline Simo synthesized VO$_2$(A) nanobelts displaying room temperature H$_2$ sensitivity as low as 0.17 ppm [162]. Additionally, Yin Haihong et al fabricated two humidity sensors based on VO$_2$(B) and VO$_2$(M) nanoflowers adapting to different relative humidity [163, 164].

Apart from the liquid synthesis methods mentioned previously, some other solid phase ways such as atomic layer deposition and chemical vapor deposition also occupy a significant share which usually are used to fabricate multilayer structure. Yang et al coated TiO$_2$ layer on VO$_2$ nanoparticles to protect VO$_2$ from being oxidized by atomic layer deposition as shown in figure 11(c) [165]. By using chemical vapor deposition, the TiO$_2$/VO$_2$ layered structure prepared by Top showed fine crystal grains as we can see the SEM morphology in figure 11(d) [166]. And as Powell demonstrated (figure 11(e)), the change in the contact angle of a water droplet on the film surface is often used to demonstrate the level of photocatalysis which induces photo-induced super hydrophilicity phenomenon. It can be seen that the TiO$_2$ layer could degrade the stearic acid which was considered as a model organic pollutant through photocatalysis after 1 h under UV irradiation, achieving a function of self-cleaning [167].
Table 1. Summary of actuators and sensors prepared by pulsed laser deposition, sputtering or vapor transport (D: displacement, L: length, RT: room temperature).

| Method               | Condition                                      | Composition          | Performance                      | Reference |
|----------------------|------------------------------------------------|----------------------|----------------------------------|-----------|
| Pulsed Laser Deposition | Temperature: $-500 \degree C$, Pressure: 10–50 mTorr, Target: V/VO$_2$ | VO$_2$/SiO$_2$ Cantilever | D: 82 $\mu$m, D/L: 0.15, Response time: 0.34 ms | [42]      |
|                      |                                                | SWNT/VO$_2$/SiO$_2$ Cantilever | D: 50 $\mu$m, D/L: 0.125, Response time: 3.3 ms | [37]      |
|                      |                                                | Cr/VO$_2$ Nanocoil (Micromuscle) | L: 200 $\mu$m, Response time: 830 $\mu$s | [49]      |
|                      |                                                | Cr/VO$_2$ Cantilever (Micropalm) | D: 36 $\mu$m, D/L: 0.6, Response time: $\sim$160 $\mu$s | [48]      |
| Sputtering           | Temperature: $-500 \degree C$, Pressure: 5–10 mTorr, Target: V/V$_2$O$_5$ | CNT/VO$_2$ Cantilever | D: 670 $\mu$m, D/L: 0.39, Response time: $\sim$12.5 ms | [36]      |
|                      |                                                | CNC/VO$_2$ Nanocoil | D: 20 $\mu$m, D/L: 0.4, Response time: 106 $\mu$s | [47]      |
|                      |                                                | Cr/VO$_2$ Microtube | D: $\sim$100 $\mu$m, D/L: $\sim$1, Diameter: 30 $\mu$m | [46]      |
|                      |                                                | VO$_2$ Helix | D: $\sim$30 $\mu$m, D/L: 0.2, Diameter: 30 $\mu$m | [153]     |
| Vapor Transport      | Temperature: 650–1000 $\degree C$, Pressure: 1 atm or few Torr, Source: VO$_2$/V$_2$O$_5$ | VO$_2$ nanobeam (Strain sensor) | Bias: 1 V, Strain: 0.25%, (RT) Response time: $<5$ s | [57]      |
|                      |                                                | VO$_2$ nanowire (H$_2$ sensor) | Bias: 10 V, Flux: 5 sccm, (55 $\degree C$) Response time: tens of seconds | [50]      |
|                      |                                                | VO$_2$ nanorod (CH$_4$ sensor) | Concentration: 500 ppm, (RT) Response time: 75 s | [52]      |
|                      |                                                | VO$_2$ nanowire (He sensor) | Pressure: 100 Torr, (RT) Response time: tens of seconds | [54]      |

These miscellaneous methods provide their own advantages for our demands such as large-scale, low-cost, co-doping, multilayer, and can achieve various morphologies by changing the ratio of precursors and other conditions. Thus, the VO$_2$ synthesized by these methods can meet the requirements of all kinds of applications.

7. Conclusions and outlook

VO$_2$ has been a forefront of actuator, sensor, switch, smart window, energy storage because of its fascinating properties such as giant change of IR-transmission, resistivity, shape-changing and during ultrafast phase transition at $68 \degree C$. As the fabrication technology develops rapidly, high quality VO$_2$ nanoparticle, nanobeam and nanomembrane have been synthesized successfully. Together with application of lithography, focused ion beam, microelectromechanical systems and self-rolling, extraordinary microactuator, 3D reconfigurable device, high-sensitivity sensor have sprung up in the past decade years. In this review, we detailed three popular methods including vapor transport, PLD and sputtering. Among these, vapor transport is a prominent method for preparation of single crystal VO$_2$ nanobeam which is generally applied in sensor device, while the PLD and sputtering are suitable for VO$_2$ film and sputtering is especially capable of preparation of large-scale area film. Then some typical actuators and sensors based on these methods are summarized in table 1. One can see that VO$_2$ plays an indispensable role in the devices’ functional performance. All the actuators from micro-scale to millimeter-scale demonstrate giant displacement and response time which lay the foundation for smart MEMS, micro-robots, biomimetic devices and so on. The single crystal VO$_2$ sensor with different length show divers detect species and high sensitivity. Additionally, thanks to the convenient manipulation of the above-mentioned methods, VO$_2$ can be doped and decorated easily during fabrication process which can further regulate lattice structure, stress state and composition achieving adjustable MIT temperature, phase state, conductivity, hysteresis width, etc.

There are still rooms for progress for fabrication methods and application of VO$_2$ devices. For instance, most of the nanomembrane preparation need post-annealing procedure which exhausts energy consumption and wastes time. It is necessary to enhance both density and area of crystallization to simplify the whole process. Further, there is necessary to control the size, position, and order of one-dimensional
nanobeam artificially. For the actuator and sensor, ongoing efforts should be put to attain quicker response times and more stable sensitivity. In order to serve more practically, the MIT temperature should be modified more precisely and more closed to room temperature. However, these drawbacks would be solved one day so long as we carried out joint efforts. VO₂ devices will be optimized continuously to benefit mankind and serve our society all along.

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