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

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Abstract

Vanadium dioxide (VO₂) receives a great deal of attention because of its intriguing properties of metal-insulator transition and its wide applications in electronics, optoelecronics, smart coatings, and so on. To further enhance the performance of their applications, low dimensional VO₂ 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 VO₂ nanomaterials are discussed, focusing on their preparation methods, properties, and applications, as well as the existing challenges and future prospectives.

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]. VO₂ attracts numerous research interests in the aspects of strongly correlated oxide, semiconductor, transition metal oxide and phase transition materials since VO₂ 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 VO₂, it is more convenient to control the temperature artificially by stress, doping and geometrical structure design. During the MIT, VO₂ 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 VO₂ 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 VO₂ 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 VO₂ 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 [57]. (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.



Figure 2. (a) Resistance changes during MIT [46]. (b) Scheme of VO_2 crystal structure of metallic (tetragonal) and insulating (monoclinic) states (yellow ball: V atom; blue ball: O atom). (c) Electronic band structure in metallic (right) and insulating (left) states [102]. (d) Infrared images of the nearfield scattering amplitude show percolation transition (metallic phase: light blue and white, insulating phase: dark blue) [107].

2. The phase transition of VO₂

The mechanism of the VO₂ phase transition has been studied for decades. As we know, polycrystalline VO₂ film will have 3–4 order change of the resistance as shown in figure 2(a) [46], and for single crystal VO₂, 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]. VO₂(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 VO₂ phase transition critical temperature (~68 °C), the distorted rutile structure changes to tetragonal structure VO₂(R) where V⁴⁺ 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 VO₂ 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_{II} band into fully occupied and the anti-bonding. Meanwhile, the π^* orbitals move to higher energies being empty. Thus, there is an e.g. ~0.6–0.7 eV bandgap between d_{II} band and π^* band where the Fermi energy exists and now VO₂ performs as an insulator. While after the MIT, the VO₂(R) whose Fermi energy state falls between the d_{II} orbitals and anti-bonding π^* orbitals showing the metallic characteristics [102, 109–111].

Although the electric band and MIT behavior of VO2 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 VO₂ 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 VO2 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 singe 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 VO_2 nanobeams as shown in figure 3(b). The well-prepared one-dimensional nanowires were grown under temperature T = 900–1100 °C, pressure P = 12–13 Torr and time t = 5 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 VO_2 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 V₂O₅ 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 V_2O_5) melt and aggravated into microscopic droplets. As the temperature rose, the new phase (VO_2) created at the developing apex of the nanobeams with the feeding materials supplied via the peripheral liquid wetting layer (V_2O_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 μ 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: V₂O₅ powder, evaporation temperature: ~880 °C, Ar flow rate: ~6.8 sccm, pressure: ~5 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 V₂O₅ 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 VO₂ nanobeams

As the VO₂ 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 VO₂ 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 V⁴⁺ with W⁶⁺ 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 VO₂ 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 H2, Ar and CH4. Continuous efforts have been concentrated on the improvement of sensitivity and selectivity such as decorating VO₂ 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, VO₂ 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 μ m [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 M₁-M₂ phase evolution in a single end-clamped VO₂ nanobeam subjected to tensile and compressive stress. Previous works have proved the stabilization of the M₂ phase by applying uniaxial compressive strain in the [110] direction in pure VO₂. Thus, as shown in figure 5(d), with the uniaxial tensile strain along the c_R direction, the fraction of the M₂ phase increased in order to release the strain in the nanobeam. And the relatively high electrical resistance of the M₂ phase compared to the M₁



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 VO₂ 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 VO₂ nanowire has high sensitivity, quick response time and good reproducibility at room temperature.

4. Pulsed laser deposition

4.1. Fabrication of VO₂ 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 natures 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 VO_2 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 VO_2 film deposited on a sapphire substrate, showing that the grains have an irregular shape with a grain size of less than 0.5 μ m. 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 V_2O_5 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 VO_2 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 VO_2 film which is suitable for micro-scale devices. In this regard, Nelson



Figure 7. (a) SEM image of SWNT/VO₂ film. The scale bar is 500 nm. (b) Schematic diagram of SWNT/VO₂ cantilever. (c) Displacement and response time of SWNT/VO₂ and VO₂ cantilever under low laser power [37]. (d) SEM cross-section image of a VO₂ film deposited on SiO₂/Si substrate. The scale bar is 500 nm. (e) The large bending amplitude of Cr/VO₂ bimorph during MIT. The scale bar is 50 μ m. (f) Actuating the entire micropalm by laser [48]. The scale bar is 50 μ m. (g) SEM cross section image of 30 nm VO₂ nanomembrane [134]. (h) Temperature dependence of the emittance for 1.0 at.% W doped VO₂-based device [135].

group did lots of researches on VO₂ cantilever microactuator mostly based on this method. They created a preliminary microactuator based on VO₂/Si cantilever in 2009 whose length was 350 μ m with 115 μ m 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 μ m [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 VO₂ [37], they prepared ~120 nm thick VO₂ 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/VO₂ cantilever (shown in figures 7(a) and (b)). It was found that larger displacement could be produced under low laser power (compared to pure VO₂ 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 VO₂ 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 μ m), high-work density (0.63 mJ cm⁻³) VO₂ 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 VO₂ target. Cr layer was deposited on the VO₂ to form stress difference. The prepared film SEM cross-section as shown in figure 7(d). And after photolithography and etching the SiO₂ under the VO₂, 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 VO₂ 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 VO₂ 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 VO₂/Al systems behave increasing emissivity with higher temperature, which is good for the spacecraft to maintain its temperature by adapting the radiated heat of VO₂. This is attributed to the high IR reflectivity of Al substrate compared to quartz or silicon [136]. Then, Hendaoui employed W doped VO₂/SiO₂/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 VO₂ 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.



Figure 8. (a) Electrical conductivity plotted for DC sputtered VO_2 [88]. (b) SEM image of VO_2 film with an average power of 600 W prepared by Aijaz [144]. (c) AFM image shows the surface morphology of VO_2 prepared by Fortier [87]. (d) Schematic illustration of DC magnetron sputtering deposition apparatus. (e) Schematic illustration of modified DC magnetron sputtering for co-doping.

5. Sputtering

5.1. Fabrication of VO₂ 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 VO₂ target to prepare VO₂ 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 VO₂ 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 5×10^{-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 $^{\circ}$ C using an optimized O₂ 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 VO₂ 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 VO₂ 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 VO₂ film and doped VO₂ 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 VO₂ 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 VO₂ 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 VO₂ 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 VO₂ appeared during an oxygen percentage of 15–25%. When the oxygen fraction beyond 30%, much more oxygen leads to the form of V₂O₅. 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 < T < 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 < T < 570 °C, the films consisted of oriented, columnar grains with large and well-defined grains displayed the best optical and electrical switch at 505 °C < T < 570 °C. From the discussed above, we can conclude that proper sputtering condition plays a decisive role in VO₂ 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 VO₂ nanomembranes

Sputtering is widely used in the fabrication of VO₂ film along with the sputtering technology become mature gradually. He Ma *et al* developed flexible, all-inorganic actuators based on bimorph structures composed of VO₂ and carbon nanotube (CNT) thin films [36]. The driving force of VO₂/CNT actuators originates from the MIT of VO₂ triggered thermally by external stimuli as illustrated in figure 9(a). They found that VO₂ is orientated along the (011) plane on CNT films preferentially, so the c_R axis of VO₂ generally sits in the plane of VO₂/CNT films. When heated beyond the MIT temperature, VO₂ shrinked along the in-plane direction and VO₂/CNT cantilever to bend toward the VO₂ side. And we can see that the tip displacement could reach



Figure 9. (a) Schematic of a VO₂/CN1 actuator responding to external stimuli. (b) The movement of VO₂/CN1 actuator from 60 °C to 78 °C [36]. (c) Schematic of a VO₂/CNC actuator responding to external stimuli. (d) The deformation of VO₂/CNC under temperature change of 10 °C [47]. (e) Schematic diagram of self-rolling process of Cr/VO₂ microtube. (f) The I–V curve of different diameters of Cr/VO₂ microtubes [46]. (g) Schematic illustration of VO₂ microhelix triggered by laser reversely. The scale bar is 30 μ m. (h) Corresponding optical image of microhelix triggered by laser [153].

800 μ m under $\Delta T = 18$ °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 μ m 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 μ m⁻² reversely. And the deformation at about 30 μ m 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(ethyleneterephthalate) (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



 VO_2 on copper and the right is the real smart window film [20]. (b) The millimeter-scale CNT/VO₂ actuator from side view. (c) The CNT/VO₂ actuator bend with giant amplitude triggered by laser. (d) The biomimetic hand made by CNT/VO₂ actuator. (e) The biomimetic hand can grab when laser is on [36]. (f) The cross sectional TEM image of thick VO-MO film on Si. (g) Reflectance of different thickness VO-MO films on quartz [137].

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 VO_2 preparation by Greenburg in 1983 who fabricated pure VO_2 and doped with tungsten, molybdenum or



bilayer films [167].

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 VO₂ 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 VO₂-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 °C and low solar absorptance 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 VO₂(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 VO₂@TiO₂ nanorod structure as shown in figure 11(a) which combine the modulation ability for IR light of VO₂ and the photocatalysis for organic dye of TiO₂. 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 VO₂ a good candidate for humidity and gas sensing. For example, Zhu Hongmei *et al* studied the gas sensing behavior of the flowerlike VO₂(B) powders toward a variety of flammable and toxic gases such as ethanol, acetone, butanol and isopropanol [161]. Aline Simo synthesized VO₂(A) nanobelts displaying room temperature H₂ sensitivity as low as 0.17 ppm [162]. Additionally, Yin Haihong *et al* fabricated two humidity sensors based on VO₂(B) and VO₂(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 TiO₂ layer on VO₂ nanoparticles to protect VO₂ from being oxidized by atomic layer deposition as shown in figure 11(c) [165]. By using chemical vapor deposition, the TiO₂/VO₂ 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 TiO₂ 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].

| Method | Condition | Composition | Performance | Reference |
|----------------------------|---|--|--|-----------|
| Pulsed Laser Deposition | Temperature: ~500 °C, Pressure: 10–50 mTorr, | VO ₂ /SiO ₂ Cantilever | D: 82 μm, D/L: 0.15, Response time: 0.34 ms | [42] |
| | Target: V/VO ₂ | SWNT/VO ₂ /SiO ₂ Canti- lever | D: 50 μ m, D/L: 0.125, Response time: 3.3 ms | [37] |
| | | Cr/VO ₂ Nanocoil (Micromuscle) | L: 200 μm, Response time: 830 μs | [49] |
| | | Cr/VO ₂ Cantilever (Micropalm) | D: 36 μm, D/L: 0.6, Response time: ~160 μs | [48] |
| Sputtering | Temperature: ~500 °C, Pressure: 5–10 mTorr, Target: V/V ₂ O ₅ | CNT/VO ₂ Cantilever | D: 670 μm, D/L: 0.39, Response time: ~12.5 ms | [36] |
| | | CNC/VO ₂ Nanocoil | D: 20 μm, D/L: 0.4, Response time: 106 μs | [47] |
| | | Cr/VO ₂ Microtube | D: ~100 μm, D/L: ~1, Diameter: 30 μm, | [46] |
| | | VO ₂ Helix | D: ~30 μm, D/L: 0.2, Diameter: 30 μm | [153] |
| Vapor Transport | Temperature: 650– 1000 °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 °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] |

 Table 1. Summary of actuators and sensors prepared by pulsed laser deposition, sputtering or vapor transport (D: displacement, L: length, RT: room temperature).

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 VO₂ synthesized by these methods can meet the requirements of all kinds of applications.

7. Conclusions and outlook

VO₂ 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 °C. As the fabrication technology develops rapidly, high quality VO₂ 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 VO₂ nanobeam which is generally applied in sensor device, while the PLD and sputtering are suitable for VO₂ 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 VO₂ 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 VO₂ sensor with different length show divers detect species and high sensitivity. Additionally, thanks to the convenient manipulation of the above-mentioned methods, VO₂ 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 VO₂ 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. VO_2 devices will be optimized continuously to benefit mankind and serve our society all along.

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