Tuning the Doping Ratio and Phase Transition Temperature of VO₂ Thin Film by Dual-Target Co-Sputtering

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Abstract: A new simple way for tuning the phase transition temperature (PTT) of VO₂ thin films has been proposed to solve the problem of changing the doping ratio by using the dual-target co-sputtering method. A series of samples with W doping ratios of 0%, 0.5%, 1%, 1.5% and 2% have been fabricated by sputtering V films with the power of pure and 2% W-doped V targets from 500 W: 0 W, 500 W: 250 W, 500 W: 500 W, 250 W: 500 W to 0 W: 500 W respectively and then annealed in an oxygen atmosphere to form VO₂. The XRD results of both pure and W-doped VO₂ samples reveal that VO₂ forms and is the main component after annealing. The PTT can be tuned by controlling the sputtering power ratio of the pure and doped targets. It can be tuned easily from 64.3 °C to 36.5 °C by using the pure and 2% W-doped targets for demonstration, with W doping ratios from 0% to 2%. It is also valid for other doping elements and is a promising approach for the large-scale production of sputtering.

Keywords: VO₂; thin films; doping; co-sputtering; phase transition

1. Introduction

Vanadium dioxide (VO₂) has been extensively studied in the last few decades because it has a metal-insulator transition (MIT) at about 68 °C [1], which results in changes in both its electrical and optical properties. An MIT near room temperature (RT) makes a good candidate material for a wide range of applications, such as uncooled infrared (IR) detector [2], optical switching [3] and ‘smart window’ which can be used to control the room temperature intelligently for energy-saving [4].

However, many of the above applications need VO₂ to work at near RT to have high efficiency and good performance. Therefore it is important to lower the phase transition temperature (PTT) of VO₂, and many efforts have been made to do so. The PTT can be influenced and tuned by grain size [5,6], stress [7], nanostructure [8,9], and so forth. However their controllability and repeatability is low. Recently it was reported that the PTT of VO₂−ₓ thin films on sapphire can be tuned by the O₂
V metal thin films are coated by a homemade large area magnetron sputtering system without heating. The films can be deposited at a temperature of 400 °C [5]. It is difficult to heat the whole chamber of an industrial magnetron sputtering coating system and keep its vacuum. They are valid for sapphire substrates, but have not been demonstrated on amorphous glass substrates. Liu et al. reported a new approach for tuning PTT of VO2 thin films simply by annealing in atmosphere, which works on both crystalline and amorphous substrates [12]. The PTT can be easily tuned from the intrinsic temperature to 40.2 °C by tuning the annealing oxygen pressure with an RT sputtering. However it still cannot be as low as the RT of 25 °C.

Doping is another effective method for tuning the PTT of VO2. It can tune the PTT in a wide range. Doping elements such as W [13], Mo [14], Ti [15], and Ni [16] were studied extensively. The PTT can be reduced to as low as 20 °C by doped W [17–19]. However, it is difficult to change the doping quantity arbitrarily and continuously, especially for the sputtering method which is one of the best industrialized fabrication techniques. For sputtering, changing the doping element or ratio needs a new large-area target.

In this paper, we present a new approach to fabricate the doped VO2 thin films by dual-target co-sputtering without heating, which can tune the doping ratio and resultant PTT according to requirements. It is demonstrated with W-doped VO2 thin films and is valid for other doping elements.

2. Experimental Procedure

VO2 thin films can be fabricated in two steps using the dual-target co-sputtering method. Firstly, V metal thin films are coated by a homemade large area magnetron sputtering system without heating. Then they are oxidation annealed by controlling the oxygen pressure. The films can be doped by dual-target co-sputtering as shown in Figure 1. One target is pure V and the other is the doped one. The doping element or mixed elements can be pre-made in the doped target with maximum doping ratio. The pure or maximum doped VO2 thin film can be fabricated by sputtering the single target of pure or maximally doped V target, respectively. VO2 thin film with other doping ratios can be fabricated by sputtering both of the targets simultaneously. The doping ratio can be tuned by controlling the sputtering power of each target, and do not need any new targets with different doping ratios. One can obtain VO2 thin film doped with another element or mixed elements simply by changing the target with the desired elements. Such a method can even be used to fabricate VO2 thin films with different elements’ co-doping ratios. Thus it is a highly flexible deposition method.

![Figure 1. Schematic diagram of fabricating W-doped V thin films with the dual-target co-sputtering method. A pure and a W-doped V targets were used in the co-sputtering procedure. The resultant co-sputtered thin film was oxidation annealed by controlling the oxygen pressure to form the W-doped VO2 thin film.](image-url)
In this paper, W-doped VO$_2$ thin films with different doping ratios were fabricated by dual-target co-sputtering as examples. The planar metal targets with sizes of 300 mm $\times$ 140 mm were used as the cathode. W-doped V film was deposited by dual-target co-sputtering method without heating. A pure V target (with purity of 99.99%) and a W-doped target (with V: W atom ratio of 98:2) was sputtered at the same time. Different doping concentrations can be achieved by adjusting the sputtering power of each target. Power control mode is selected in the sputtering process. The cleaned substrate was placed in the chamber of the magnetron sputtering coating system and vacuumed to lower than 9.9 $\times$ 10$^{-4}$ Pa. The substrate can be amorphous glass or crystalline sapphire which is amorphous K9 glass in this work. The maximum size of samples was 200 mm square which is only confined by the size of the deposition chamber. Argon gas with a flow rate of 50 sccm was injected into the coating chamber as working gas and kept the working pressure at about 2.1 $\times$ 10$^{-2}$ Pa. The sputtering power was set to 500 W, which was increased from 0 W to 500 W at a rate of 100 W per minute. The cathode voltage was 322 V. The powers of V target and W-doped V target were set as 500 W: 0 W, 500 W: 250 W, 500 W: 500 W, 250 W: 500 W, 0 W: 500 W, respectively. The targets were sputtered for 30 min before sputtering onto the substrate. The deposition temperature was 25 $^\circ$C without need to heat the substrate. The substrate moved backward and forward underneath the targets at a constant speed of 1 m per minute, to ensure homogeneity when sputtering. The W-doped V films with different doping ratios were prepared by the above process. The sputtering power deviation is less than 340 V $\pm$ 5 V and corresponds to a maximum error of 1.5%. Since the sputtering rate of the two targets is proportional to the power, the deposition ratio of V and W-doped V is calculated to be 2:1, 2:2 and 1:2 for power ratios of 500 W: 250 W, 500 W: 500 W and 250 W: 500 W, respectively. The powers of 500 W: 0 W and 0 W: 500 W correspond to samples of pure and 2% W-doped V thin films, respectively. Therefore, the amount of W-doping in the samples prepared at the corresponding power ratio is 0%, 0.5%, 1%, 1.5%, 2%, respectively, since the V: W atom ratio of W-doped V target is 98:2. Five ratios of W-doped V films were fabricated for demonstration by tuning the power of the two targets.

The resultant films were annealed in a 250 mm diameter tubular vacuum annealing furnace. It was evacuated down to 1.5 Pa by a mechanical pump to remove the air in it. The above films were treated for heating, annealing and cooling stages to form VO$_2$ films. The annealing temperature and time were 530 $^\circ$C and 30 min, respectively. Oxygen (99.999%) was used only in the annealing stage with a flow rate of 20 sccm to ensure the oxygen pressure stayed at 18 Pa. The pressure of oxygen in the furnace was precisely controlled by a mass flow controller and monitored by a vacuum gauge.

Scanning electron microscopy (SEM, FEI SIRION 200, Hillsboro, OR, USA) was used to observe the surface micrograph of the films. The crystalline structures of the films were characterized by using X-ray diffraction (XRD, BRUKER AXS series D8 ADVANCE, Karlsruhe, Germany) with Cu-K$\alpha$ radiation, 40 kV/40 mA, 0.02$^\circ$ 2$\theta$ step size and scan time of 0.2 s per step in the range of 10$^\circ$–70$^\circ$ 2$\theta$. Near-infrared transmission spectra of V thin films with different doping ratios were characterized by a NIR2500 infrared fiber optic spectrometer from Ideaoptics Inc. (Shanghai, China) at different temperatures.

3. Results and Discussion

In order to keep the comparability of the fabricated films and increase the efficiency, a combinatorial deposition method [20–23] has been introduced to fabricate a series of V thin films with different thicknesses. The mask plates with different windows help the selective deposition on a substrate. $2^n$–1 thicknesses can be realized by only $n$ times of sputtering. The total thickness of film sputtered with 5 cycles (a single cycle is defined as once the substrate moves backward and forward underneath the targets one time) was 45 nm obtained by the cross-section of SEM, and the thickness of each sputtering cycle was deduced from the result. Here V thin films were coated three times with thicknesses of 9 nm, 18 nm and 36 nm respectively for the combinatorial deposition technique. Then 7 V film samples with thicknesses of 9 nm, 18 nm, 27 nm, 36 nm, 45 nm, 54 nm, and 63 nm were obtained. The uniformity of VO$_2$ thin film over the maximum size of 200 mm $\times$ 200 mm is good which can be seen from the photo presented in reference [24].
The micro-structure of pure and 2% W-doped V films was observed by SEM before and after annealing for comparison. The SEM images are presented in Figure 2. Nano-sized grains are uniformly distributed over the entire substrate before annealing. It is almost the same for both the pure and 2% W-doped V films. The distinctive morphological changes have been observed after the annealing process. Many grains exist on the film of pure ones after being annealed in oxygen. Most of them are larger than 100 nm. For the 2% W-doped one, a similar amount of grains was present with sizes of ten nanometers, which are much smaller than the pure one. The difference might be ascribed to the restraint of grain growth by the doping element of W [12]. It will definitely influence the optical and electrical properties of the vanadium oxide thin films. The XRD curves of pure and W-doped VO$_2$ samples are presented in Figure 3. Both the pure and W-doped VO$_2$ samples have obvious VO$_2$ and V$_2$O$_5$ diffraction peaks. There is also one weak V$_6$O$_{11}$ diffraction peak present in the W-doped samples. No other vanadium oxide peaks have been observed. This is because the W atoms replace some V atoms in the VO$_2$ polycrystalline film in the form of W$^{6+}$ and form a V$_{1-x}$W$_x$O$_2$ solid solution [25].

The diffraction peaks of XRD results agree well with the standard cards. The largest deviation of 1.4% comes from the first peak of V$_2$O$_5$ at 12.404 degrees from the standard card. The slight deviation of V$_2$O$_5$ peak at 29.14 degrees may be ascribed to the difference between our fabrication method and the method from the standard card. Different oxides and orientations observed should be ascribed to the fabrication of thin films on amorphous substrates of K9 glass.

![Figure 2. SEM surface micrographs of pure and 2% W-doped V films before and after annealing.](image)

(a) V (Before annealing)  
(b) V$_{0.99}$W$_{0.01}$ (Before annealing)  
(c) VO$_2$ (After annealing)  
(d) V$_{0.99}$W$_{0.01}$O$_2$ (After annealing)

Figure 2. SEM surface micrographs of pure and 2% W-doped V films before and after annealing. (a) Pure V film before annealing. (b) 2% W-doped V film before annealing. (c) Pure V film after annealing. (d) 2% W-doped V film after annealing. The films were sputtered with the power of 500 W: 0 W and 0 W: 500 W for the pure and 2% W-doped V targets without heating, respectively. They were annealed at 530 °C for 30 min with oxygen pressure of 18 Pa.

The modulation ability of VO$_2$ thin films on infrared transmission is critical for its application as intelligent energy-saving glass. It is studied by measuring the transmission spectra before and after phase transition. The results of 0%, 1% and 2% W-doped VO$_2$ films are shown in Figure 4, corresponding to VO$_2$, V$_{0.99}$W$_{0.01}$O$_2$ and V$_{0.98}$W$_{0.02}$O$_2$ respectively. For the test error, the signal-to-noise ratio (SNR) of the test spectrum is larger than 10,000 for all the spectral measurements and is good enough. When temperature is lower than the PTT, the films are in the insulation phase and have high infrared transmissions of 49.8%, 57.9% and 52.8% at the wavelength of 2400 nm. They will drop to 18.8%, 14.9% and 10.8% when the temperature is higher than the PTT, because they will change to metal phase with high carrier concentration. Therefore, the infrared transmission changes of pure VO$_2$ thin film, 1% and 2% W-doped VO$_2$ films are
The micro-structure of pure and 2% W-doped V films was observed by the SEM images. Nano-sized grains are uniformly distributed over the entire substrate before annealing. It is almost the same for both the pure and 2% W-doped V films. The distinctive morphological changes have been observed after the annealing process. Many grains exist on the film of pure ones after being annealed in oxygen. Most of them are larger than 100 nm. For the 2% W-doped one, a similar amount of grains was present as well.

The XRD curves of pure and W-doped VO$_2$ samples are presented in Figure 3. Both the pure and W-doped VO$_2$ samples have obvious VO$_2$ and V$_2$O$_5$ diffraction peaks. There is also one weak V$_6$O$_{11}$ diffraction peak present in the W-doped VO$_2$ samples. The distinctive morphological changes have been observed after the PTT. Both the room temperature and high temperature transmission spectra of them are larger than 100 °C was observed at 4000 cm$^{-1}$ for the 0.5% W-doped one [26]. Piccirillo et al. used the aerosol assisted chemical vapor deposition method to deposit W-doped vanadium dioxide thin films and observed noticeable changes of transmittance up to about 30% at 2500 nm [27].

![XRD curves of pure and W-doped VO$_2$ films](image)

**Figure 3.** XRD curves of pure and W-doped VO$_2$ films fabricated on amorphous K9 glass substrates. The films were sputtered with the power of 500 W: 0 W and 0 W: 500 W for the pure and 2% W-doped V targets without heating, respectively. They were annealed at 530 °C for 30 min with oxygen pressure of 18 Pa.

![Transmission spectra of pure VO$_2$, V$_{0.99}$W$_{0.01}$O$_2$ and V$_{0.98}$W$_{0.02}$O$_2$ films](image)

**Figure 4.** Visible and near-infrared transmission spectra of pure VO$_2$, V$_{0.99}$W$_{0.01}$O$_2$ and V$_{0.98}$W$_{0.02}$O$_2$ films before (10 °C) and after (100 °C) PTT, respectively. The films were annealed at 530 °C for 30 min with oxygen pressure of 18 Pa.

In the visible range, the transmission spectra of the pure and W-doped VO$_2$ films stay almost the same when wavelength is shorter than 440 nm, and have a small difference between 440 and 820 nm before and after the PTT. Both the room temperature and high temperature transmission spectra of doped VO$_2$ films in the visible spectrum are a little lower than those of pure VO$_2$ film.
The hysteresis loop of VO₂ is an important way to study its phase transition process. Figure 5 shows an optical thermal hysteresis loop of the V₀.₉₉W₀.₀₁O₂ film at 2000 nm, which is a result of the phase transition of VO₂. The transition decreases with the increase of temperature when heating, and increases with the decrease of temperature when cooling. The PTT (Tᵢ) of the VO₂ thermochromic films is defined to be \( Tᵢ = (Tᵢ,h + Tᵢ,c)/2 \), where \( Tᵢ,h \) and \( Tᵢ,c \) are the PTTs when heating and cooling, respectively [12]. The \( Tᵢ,h \) \( Tᵢ,c \) and corresponding \( Tᵢ \) are 48 °C, 38 °C and 43 °C, respectively.

![Thermal hysteresis loop of V₀.₉₉W₀.₀₁O₂ film at 2000 nm.](image)

**Figure 5.** Thermal hysteresis loop of V₀.₉₉W₀.₀₁O₂ film at 2000 nm. The black curve indicates that the transition temperature is 48 °C when the sample is heated, and the red curve indicates that the transition temperature is 38 °C when the sample is cooled.

PTT is a very important parameter of VO₂ thin film. As mentioned in the experimental section, it can be tuned by changing the doping ratio which is realized by controlling the sputtering power of each target. It is 500 W: 0 W, 500 W: 250 W, 500 W: 500 W and 0 W: 500 W of pure: 2% W-doped V targets, corresponding to doping ratios of 0%, 0.5%, 1%, 1.5% and 2% respectively for demonstration. The optical thermal hysteresis loops of VO₂ films at 2000 nm with different W doping ratios are shown in Figure 6a. It can be seen that the optical thermal hysteresis loops move to lower temperatures with an increase of doping ratio. According to the definition of PTT mentioned above, it is 64.3 °C for the pure VO₂ film without doping and reduces with the increase of doping ratio. The relationship between the PTT and doping ratio of W is shown in Figure 6b. The results come from three repeated experiments and the deviation of PTT is no more than 3%. When the W doping ratio is 0.5%, the PTT decreases 9.5 °C to 54.8 °C. It is lowered to 46.2 °C when the doping ratio increases to 1%. The PTT is further reduced to 41.3 °C when the W content increases to 1.5%. The PTT is down to 36.5 °C for 2% doping ratio, which can be further lowered by using a target with a larger W doping ratio. The transition temperature is reduced to 55 °C and 35 °C with VO₂-W-1% and VO₂-W-2% respectively, which is reported by Liu et al. using the aqueous sol-gel method [13] and similar to ours for the 2% doping one. Zhang et al. reported a decrease to 55.3 °C and 45.7 °C respectively with VO₂-W-1% and VO₂-W-2% synthesized by a facile hydrothermal approach and subsequent calcination [14], which is higher than ours for the 2% doping one. Li et al. used ion beam enhanced deposition and post-annealing techniques to prepare 3% W-doped VO₂ on SiO₂ substrates which reduced the PTT of VO₂ thin films to 28 °C [19]. The PTT should decrease further if we fabricate W-doped VO₂ thin film with a higher doping ratio. According to the existing theory, the PTT of VO₂ film is reduced by W doping, which may be due to the substitution of W⁶⁺ to V⁴⁺ in d orbital. The introduction of excess electrons reduces the band gap of the d orbit and reduces the PTT [19].
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References

1. Morin, F.J. Oxides which show a metal-to-insulator transition at the neel temperature. Phys. Rev. Lett. 1959, 3, 34–36. [CrossRef]

2. Chen, X.Q.; Yi, X.J.; Yang, Y.; Li, Y. A new CMOS readout circuit for VO2-based uncooled focal polane arrays. Int. J. Infrared Millim. Waves 2006, 27, 1281–1291. [CrossRef]
3. Chen, S.H.; Ma, H.; Yi, X.J.; Xiong, T.; Wang, H.C.; Ke, C.J. Smart VO₂ thin film for protection of sensitive infrared detectors from strong laser radiation. Sens. Actuator A-Phys. 2004, 115, 28–31. [CrossRef]
4. Jin, P.; Xu, G.; Tazawa, M.; Yoshimura, K. Design, formation and characterization of a novel multifunctional window with VO₂ and TiO₂ coatings. Appl. Phys. A-Mater. Sci. Process. 2003, 77, 455–459. [CrossRef]
5. Kana, J.B.K.; Ndjakal, J.M.; Ateba, P.O.; Ngom, B.D.; Manyala, N.; Nemraoui, O.; Beye, A.C.; Maaza, M. Thermochromic VO₂ thin films synthesized by rf-inverted cylindrical magnetron sputtering. Appl. Surf. Sci. 2008, 254, 3959–3963. [CrossRef]
6. Brassard, D.; Fourmaux, S.; Jean-Jacques, M.; Kieffer, J.C.; El Khakani, M.A. Grain size effect on the semiconductor-metal phase transition characteristics of magnetron-sputtered VO₂ thin films. Appl. Phys. Lett. 2005, 87, 051910. [CrossRef]
7. Sohn, J.I.; Joo, H.J.; Kim, K.S.; Yang, H.W.; Jang, A.R.; Ahn, D.; Lee, H.H.; Cha, S.; Kang, D.J.; Kim, J.M.; et al. Stress-induced domain dynamics and phase transitions in epitaxially grown VO₂ nanowires. Nanotechnology 2012, 23, 205707. [CrossRef] [PubMed]
8. Crunteanu, A.; Givernaud, J.; Leroy, J.; Mardivirin, D.; Champeaux, C.; Orlianges, J.C.; Catherinot, A.; Blondy, P. Voltage- and current-activated metal-insulator transition in VO₂-based electrical switches: A lifetime operation analysis. Sci. Technol. Adv. Mater. 2010, 11, 065002. [CrossRef]
9. Mun, B.S.; Yoon, J.; Mo, S.K.; Chen, K.; Tamura, N.; Dejoie, C.; Kunz, M.; Liu, Z.; Park, C.; Moon, K.; et al. Role of joule heating effect and bulk-surface phases in voltage-driven metal-insulator transition in VO₂ crystal. Appl. Phys. Lett. 2013, 103, 061902. [CrossRef]
10. Jiming, B.; Lihua, M.; Shukuo, Z. Structural and optical properties of VO₂ film grown on sapphire substrate by pulsed laser deposition. Adv. Mater. Res. 2014, 912, 325–328. [CrossRef]
11. Chen, S.; Dong, C.Z.; Zhang, L.F.; Fu, Z.M. Annealing effects on W-doped VO₂ thin films prepared from magnetron sputtering. In Materials Processing Technology II, Pts 1–4; Zhao, L.C., Wang, H., Xiao, C.F., Eds.; Trans Tech Publications Ltd.: Durnten-Zurich, Switzerland, 2012; Volume 538–541, pp. 101–104.
12. Liu, X.X.; Wang, S.W.; Chen, F.L.; Yu, L.M.; Chen, X.S. Tuning phase transition temperature of VO₂ thin films by annealing atmosphere. J. Phys. D-Appl. Phys. 2015, 48, 265104. [CrossRef]
13. Liu, D.Q.; Cheng, H.F.; Xing, X.; Zhang, C.Y.; Zheng, W.W. Thermochromic properties of W-doped VO₂ thin films deposited by aqueous sol-gel method for adaptive infrared stealth application. Infrared Phys. Technol. 2016, 77, 339–343. [CrossRef]
14. Zhang, Y.F.; Li, W.; Fan, M.J.; Zhang, F.F.; Zhang, J.C.; Liu, X.H.; Zhang, H.N.; Huang, C.; Li, H.B. Preparation of W- and Mo-doped VO₂(M) by ethanol reduction of peroxovanadium complexes and their phase transition and optical switching properties. J. Alloys. Compd. 2012, 544, 30–36. [CrossRef]
15. Du, J.; Gao, Y.F.; Luo, H.J.; Zhang, Z.T.; Kang, L.T.; Chen, Z. Formation and metal-to-insulator transition properties of VO₂-ZrV₂O₇ composite films by polymer-assisted deposition. Sol. Energy Mater. Sol. Cells 2011, 95, 1604–1609. [CrossRef]
16. Miyazaki, K.; Shibuya, K.; Suzuki, M.; Wado, H.; Sawa, A. Correlation between thermal hysteresis width and broadening of metal-insulator transition in Cr- and Nb-doped VO₂ films. Jpn. J. Appl. Phys. 2014, 53, 071102. [CrossRef]
17. Jin, P.; Tazawa, M.; Ikejama, M.; Tanemura, S.; Macak, K.; Wang, X.; Olafsson, S.; Helmersson, U. Growth and characterization of epitaxial films of tungsten-doped vanadium oxides on sapphire (110) by reactive magnetron sputtering. J. Vac. Sci. Technol. A-Vac. Surf. Films 1999, 17, 1817–1821. [CrossRef]
18. Soltani, M.; Chaker, M.; Haddad, E.; Kruzelecky, R.V.; Margot, J. Effects of Ti-W codoping on the optical and electrical switching of vanadium dioxide thin films grown by a reactive pulsed laser deposition. Appl. Phys. Lett. 2004, 85, 1958–1960. [CrossRef]
19. Li, J.H.; Yuan, N.Y.; Xie, T.B.; Dan, D.D. Preparation of polycrystalline Vo.97W0.03O₂ thin films with ultra high TCR at room temperature. Acta Phys. Sin. 2007, 56, 1790–1795.
20. Wang, S.W.; Chen, X.S.; Lu, W.; Wang, L.; Wu, Y.G.; Wang, Z.S. Integrated optical filter arrays fabricated by using the combinatorial etching technique. Opt. Lett. 2006, 31, 332–334. [CrossRef]
21. Wang, S.W.; Liu, D.; Lin, B.; Chen, X.; Lu, W. 16 × 1 integrated filter array in the MIR region prepared by using a combinatorial etching technique. Appl. Phys. B-Lasers Opt. 2006, 82, 637–641. [CrossRef]
22. Wang, S.W.; Li, M.; Xia, C.S.; Wang, H.Q.; Chen, X.S.; Lu, W. 128 channels of integrated filter array rapidly fabricated by using the combinatorial deposition technique. Appl. Phys. B-Lasers Opt. 2007, 88, 281–284. [CrossRef]
23. Liu, X.X.; Wang, S.W.; Xia, H.; Zhang, X.T.; Ji, R.N.; Li, T.X.; Lu, W. Interference-aided spectrum-fitting method for accurate film thickness determination. *Chin. Opt. Lett.* **2016**, *14*, 081203. [CrossRef]

24. Liu, X.X.; Ji, R.N.; Zhang, Y.; Li, H.G.; Wang, S.W. Annealing process and mechanism of glass based VO$_2$ film from V oxidation in pure oxygen atmosphere. *Opt. Quantum Electron.* **2016**, *48*, 453. [CrossRef]

25. Li, H.Q.; He, X.X.; Liu, T.; Nie, Z.H.; Lv, X.Q. Modulus and Internal Friction of W-Doped VO$_2$ Thin Films. *Appl. Mech. Mater.* **2011**, *130*, 3343–3346. [CrossRef]

26. Li, J.; Liu, C.-Y.; Mao, L.-J. The character of W-doped one-dimensional VO$_2$ (M). *J. Solid State Chem.* **2009**, *182*, 2835–2839. [CrossRef]

27. Piccirillo, C.; Binions, R.; Parkin, I.P. Synthesis and characterisation of W-doped VO$_2$ by Aerosol Assisted Chemical Vapour Deposition. *Thin Solid Films* **2008**, *516*, 1992–1997. [CrossRef]

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