

Preparation of five oxidized vanadium two thin films by sol-gel method

Yiming Zhang *, Shuxia Wang, Juntong Yue

School of Liaoning university of science and technology, Liaoning, China.

* Corresponding Author

Abstract

Vanadium oxide is a transition metal oxide, in which V₂O₅ is the most stable and has good photoelectric properties. In this paper, tungsten doped V₂O₅ thin films were prepared by sol-gel method. The morphology and crystal phase of the films were analyzed, and the transmission spectra of the films were measured. The results show that with the increase of tungsten doping concentration (molar ratio is 0.5 - 2 mol%), the higher the light transmittance of V₂O₅ film, which can be used for the preparation of optical materials.

Keywords

Sol-gel, Vanadium pentoxide, Tungsten Doping, Vanadium oxide film

1. Introduction

Vanadium has a variety of oxides, and the color also changes with the change of valence. Generally speaking, 5 valence V is light yellow, 4 valence V is black or blue, 3 valence V is green and 2 valence V is purple. When pentavalent vanadium changes to low price, the color will change, which can be used for solar sensitized dye modification and catalysis [1,2,3]. In addition, the resistivity and transmittance of the films change before and after the phase transition, which has a good application prospect in the fields of temperature sensing, photosensitive devices and so on.

There are many methods for the preparation of V₂O₅ thin films, such as magnetron sputtering [4], sol-gel [5], chemical deposition [6], evaporation method, etc. Among them, sol-gel method has the advantages of low cost, simple operation and good uniformity. It is suitable for mass production and is widely used in coating production. In 1982, Xin [7] prepared V₂O₅ thin film by mixing V₂O₅ powder with butanol and benzyl alcohol and spin coating on indium tin oxide glass. In 2011, Riedl et al. Prepared V₂O₅ thin film by spin coating method with vanadium oxide and isopropanol solution as raw materials to construct organic solar cells. In 2017, Chen et al [8] rotated the isopropanol solution of three isopropanol vanadium electrodes on the electrode by sol-gel method and annealed 1min at 120 degree temperature to obtain V₂O₅ film. In 2018, aswani sehar et al. [9] used vanadium oxide and isopropyl titanate as raw materials, added anhydrous isopropanol solution, and obtained V₂O₅ film through coating. In 2019, ravendras rerata et al. [10] obtained V₂O₅ film by coating with V₂O₅ powder, hydrogen peroxide and deionized water.

In this paper, thin V₂O₅ films were prepared on silica glass by sol-gel method. The morphology, crystal phase and transmission spectrum of the thin films were measured by optical microscopy, XRD and Fu Liye transform spectrometer. The optical transmittance of the films can be effectively changed after the tungsten doped five oxidized two vanadium thin films.

2. Experimental method.

Quartz glass is used as the substrate, and the specification size is 2cm × 2cm × 1mm. Rapid substrate cleaning method: pour an appropriate amount of deionized water into the ultrasonic cleaning instrument, add a few drops of washing solution, and use ultrasonic cleaning for 20min; Put the quartz substrate into absolute ethanol and wash it with ultrasonic for 20 min; After putting the quartz substrate into acetone, ultrasonic cleaning for 20 min; Finally, the substrate is thoroughly cleaned with deionized water solvent and placed in the drying oven for use.

At room temperature, take four parts of 0.99g analytical pure diacetyl acetone vanadium oxide, place them in a beaker with a capacity of 100ml, add 30ml anhydrous methanol respectively and stir. Add 0.5%, 1% and 2% WCl_6 to form a dark brown solution, seal the beaker mouth with fresh-keeping film, place it in a magnetic stirrer, and prepare V_2O_5 sol precursor after 24 hours of continuous stirring and 48 hours of dark light aging. Install V_2O_5 sol spin precursor on sol spin coating machine, spin coating for 6S at 600r / s low speed, and then spin coating for 30s at 3000r / s high speed. After spin coating, put the film into a container and take it out after vacuum drying at 100 °C in a drying oven for 30min. Repeat drying for 3 times. Finally, the dry gel membrane was heated to 600 °C 30min in muffle furnace and V_2O_5 pure crystalline phase film was obtained.

The X-ray laser diffractometer (XRD) for the experiment is designed and manufactured by panaco company in the Netherlands. The model is D / max IIIc. The scanning speed is 20 ° / min, the scanning range is 10 ° - 90 °, and the accuracy is 0.01 °. We use the latest sigma500 field emission scanning electron microscope launched by Zeiss, which is designed with a mature Gemini optical system with a resolution of 0.5% 8nm@15KV, the magnification is 10-1000000*, and the acceleration voltage is 0.02-30kv. The UV-VIS Spectrometer with model code v-uv-3600 of Shimadzu company in Japan can be used to accurately test the visible luminosity and transmittance of various thin film material samples. The test speed range is generally 250~1600nm, the test operation speed is generally slow to medium speed, the test wiring mode is direct, and the slit width is 3nm. Most enterprises hold the outdated and backward concept that environmental cost control is to reduce environmental costs, and only consider the absolute reduction of environmental costs, without considering the development of circular economy or technological transformation by investing certain resources, so as to realize the recycling and efficient use of resources, and achieve a win-win situation of economic and environmental benefits and a relative reduction of environmental costs while achieving energy conservation and emission reduction. As a result, the environmental cost control method of enterprises is single and the effect is poor.

3. Results and discussion.

3.1. XRD analysis of V_2O_5 thin film.

The XRD patterns of vanadium pentoxide films with different tungsten content are shown in Fig. 2. When undoped, at 2θ = Typical diffraction peaks appear at 26.1 °, 34.3 °, 37.3 °, 51.1 °, 61.9 °, 65.8 °, and there are no other diffraction peaks. Compared with the XRD diffraction card of standard V_2O_5 (Card No.: 21033001), the above diffraction peak positions correspond to the six crystal planes (110), (310), (401), (020), (710) and (711) of the complete V_2O_5 peak positions respectively, indicating that the film has a single crystal phase and is a vanadium pentoxide film of pure orthogonal triangular system. There is no new metal diffraction peak in the tungsten doped film, which indicates that all tungsten ions have been doped into the V_2O_5 lattice [11,12], and tungsten ions have not entered the V_2O_5 lattice and no new oxides have been formed. cost.

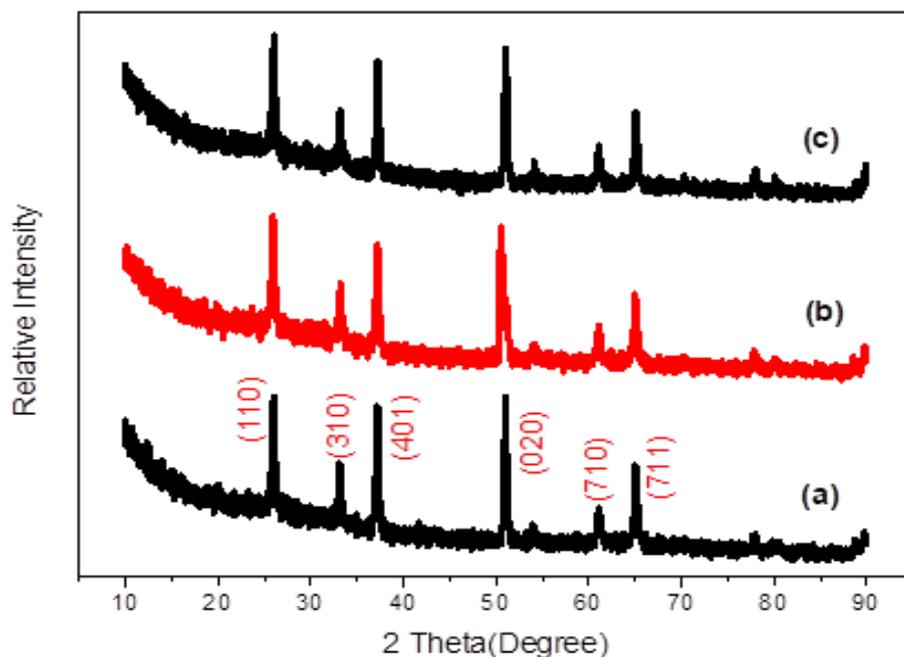


Figure 1: The XRD study of vanadium dioxide with different W / V molar ratio (a) Doping 0 (b) Doping 1% (c) Doping 2%

3.2. SEM analysis of the film.

The morphology of V_2O_5 films annealed at $600\text{ }^\circ\text{C}$ was studied by SEM image analysis. abcde in the figure corresponds to the plane SEM of vanadium pentoxide films without tungsten doping and with tungsten doping molar ratios of 0.5%, 1% and 2%, respectively. Figure(d), figure(e) and figure(f) are the high magnification diagrams when tungsten doping 2% mol. It can be seen from the figure that the doping of tungsten will have a great impact on the size of vanadium pentoxide. The vanadium pentoxide nanoparticles prepared by us have a rod-shaped structure and the particle size is about 150nm-500nm. In figure a, the average particle size of undoped vanadium pentoxide particles is about 150nm. In Figure (d), when doped with 2% mol, the average particle size of vanadium pentoxide particles is about 500nm. At the same time, we will find that amorphous phase appears on the surface of the film, And there is reunion. During the preparation of sol precursor, the particles are in a dynamically stable state, that is, the particles cannot coalesce, and the particles will remain relatively stable. When spin coating coating is carried out, the particles undergo high-speed centrifugal rotation. At this time, the colloidal particles are easy to agglomerate through diffusion movement [13]. As more and more W^{6+} enters the V_2O_5 lattice, the difference in radius between W^{6+} and V^{5+} leads to the deformation of crystal structure, It is not conducive to crystal growth and the proportion of amorphous phase increases. With the lattice distortion, the crystal arrangement is also affected, which will lead to the increase of agglomeration.

From figures (a) to (e), we can see that the vanadium pentoxide particles gradually increase with the increase of tungsten doping. In addition, because the radius of tungsten ion is larger than that of vanadium ion, and tungsten doping is actually the doping of tungsten ion into the lattice of vanadium pentoxide, doping tungsten ion will increase the particle size of vanadium pentoxide, which is consistent with the above XRD analysis that tungsten ion is doped into the lattice of vanadium pentoxide.

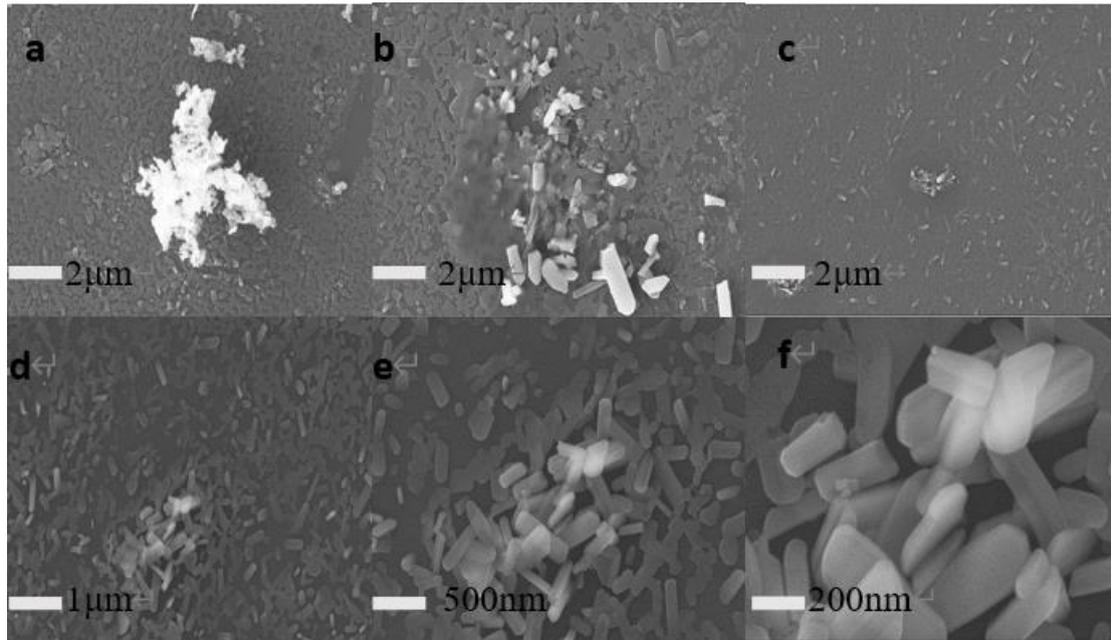


Figure 2: Front SEM of vanadium pentoxide films with different tungsten doping Amounts (a)Doping 0 mol (b)Doping 1%mol (c)Doping 1.5%mol (d)Doping 2%mol (e)~(f) Doping 2% mol high power diagram

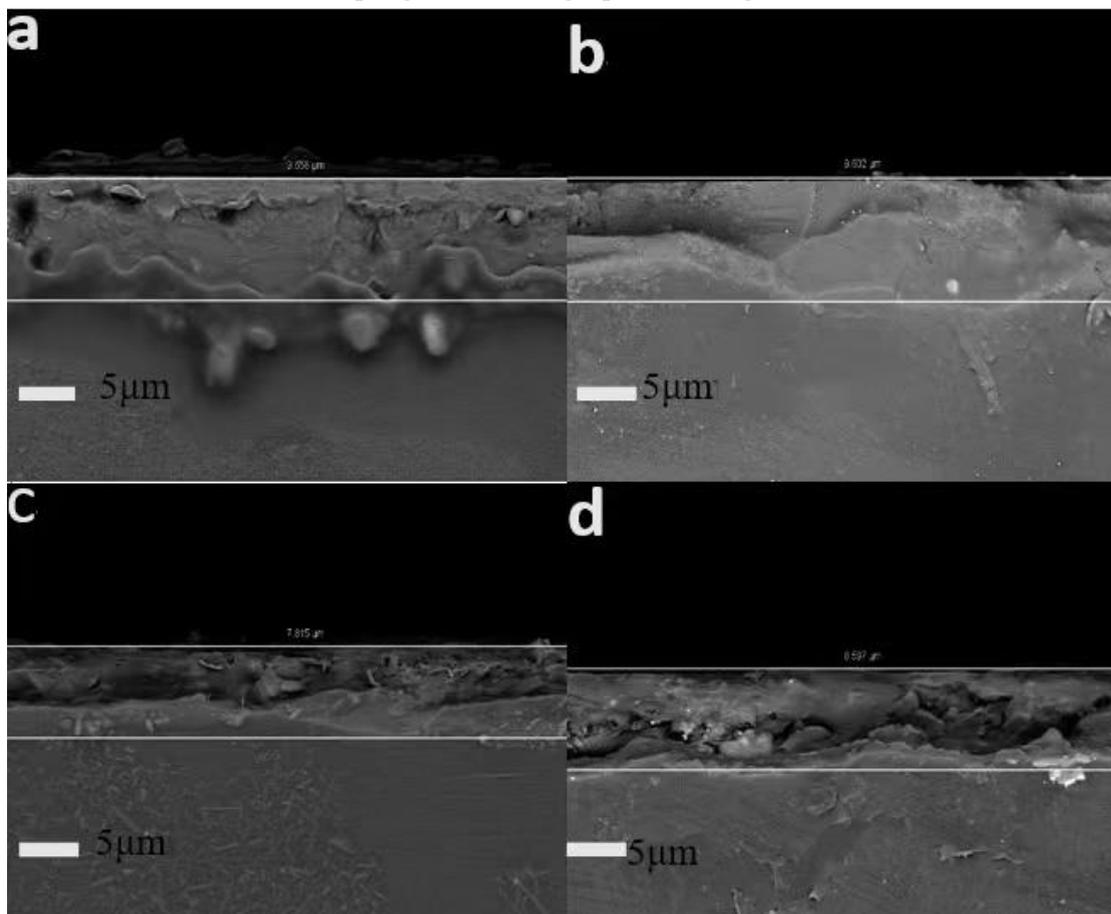


Figure 3: cross sectional SEM spectra of vanadium pentoxide films with different tungsten doping amounts. (a)Doping 0 mol (b)Doping 0.5%mol (c) Doping 1%mol (d) Doping 2%mol. For the thickness of vanadium pentoxide film, we can see from the figure that the thickness of undoped vanadium pentoxide film is 9.658 μ m. When tungsten is doped with 0.5% mol, 1% mol and 2% mol, the corresponding film thickness is 9.602 respectively μ m, 8.597 μ m, 7.815

μm . In general, the thickness of the film is basically $7.8\ \mu\text{m}$ - $9.7\ \mu\text{m}$, because the coating method used in this experiment is spin coating method. The control of film thickness cannot be completely consistent, but there is basically no difference.

3.3. Transmission spectrum analysis of thin films

Fig. 4 shows the transmission spectrum of V_2O_5 film in the band of $200 \sim 1500\ \text{nm}$. The wavelength transmission range is about $200\text{nm} \sim 420\text{nm}$. Similarly, the thin film is used as the sample. Although the optical parameters are different, the spectral optical properties of the transmittance are the same and the transmittance is low. The transmittance of the thin film sample is basically maintained between $25\% \sim 38\%$, which is due to the absorption effect of the base quartz glass on ultraviolet light wave [14]. At a given wavelength width of 350nm , the absorption peak width shows a downward linear mutation. In the short wavelength width range of $400 \sim 1300\text{nm}$, the transmittance increases significantly, and in the short wavelength width range of $1300 \sim 1500\text{nm}$, the transmittance gradually tends to be stable [15].

With the increase of tungsten doping, the transmittance of the film increases gradually with the increase of tungsten doping. Tungsten doped films can improve their absorption of transmitted light [16] by appropriately adjusting the transmission band gap [17] of doped materials. With the increase of tungsten content, the optical forbidden beam band [18] increases significantly, moves to a shorter wavelength, and the transmittance increases significantly. With the increase of tungsten doping content, the transmittance of V_2O_5 film increases significantly in the whole visible band of $400\text{-}800\ \text{nm}$; When the light wavelength is 400nm , the transmittance is 35% . With the great increase of tungsten dopant content, the transmittance in visible light band is greatly increased from 35% to 70% , which is increased by 35% . This is because the doping of tungsten ions may lead to the blue shift of the light absorption edge caused by the broadening of the band gap of the material [19,20]. Doping w ions can improve the visible light transmittance of V_2O_5 .

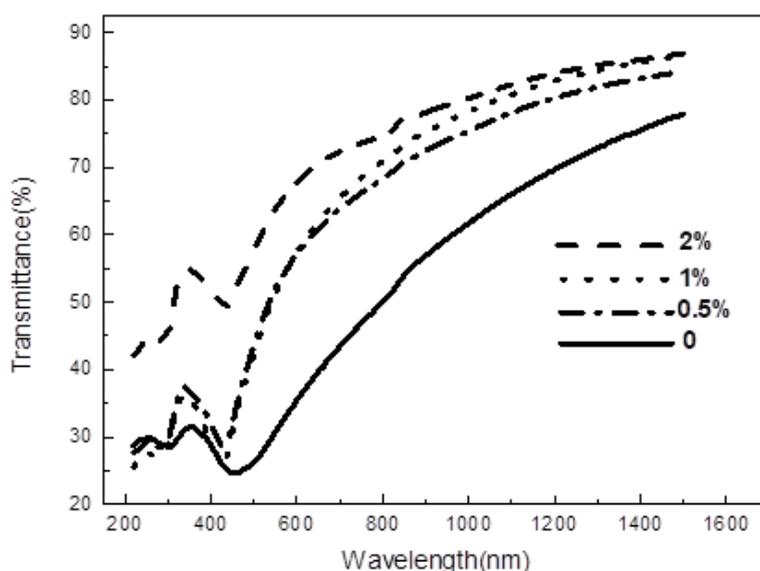


Figure4: Optical transmittance of vanadium pentoxide thin films with different tungsten doping amounts

4. Conclusion

Tungsten doped V_2O_5 thin films were prepared by sol-gel method. The morphology, phase formation and transmission spectrum of the films were measured by X ray diffractometer,

scanning electron microscope and spectrometer. The results show that tungsten doped V_2O_5 films have high transmittance and can be used in the preparation of optical transparent materials. All tungsten ions enter the vanadium pentoxide lattice. Tungsten Doped Vanadium Pentoxide film can improve the transmittance of the film, and with the increase of tungsten doping, the transmittance of the film surface also increases gradually. It will become an ideal material in the application of optical glass such as large glass curtain wall.

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