Preparation of Vanadium Oxide Thin Films under Different Annealing Conditions

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Abstract. A novel method was used to fabricate V$_2$O$_5$ thin films by combining magnetron sputtering and vacuum annealing processes on Al$_2$O$_3$ ceramic substrates, which greatly improved the success rate of the experiments and reduced the experimental requirements for the instruments. The substrate was magnetron sputter coated further oxidized in a tube furnace to produce a uniform V$_2$O$_5$ surface, then annealed at high temperatures. XRD and SEM measurements were performed on the obtained films under different annealing conditions. Characterization results of the samples indicate that the highly reproducible VO$_2$ thin films can be achieved by controlling the process parameters of the magnetron sputtering and vacuum annealing. The experimental results are of great guidance value in VO$_2$ thin film preparation.

1. Introduction

Vanadium dioxide (VO$_2$) undergoes a rapid and reversible first-order displacement metal-insulator phase transition from low-temperature insulator state to high-temperature metal state at 68°C [1]. The phase transition is reversible from monoclinic to tetragonal rutile changes [2], accompanied by changes in electronic states and crystal lattices make VO$_2$ thin film phase changes in optical properties, electrical properties magnetic properties and etc [3], so VO$_2$ in the electrical switch [4] terahertz Device [5] and smart window [6] has great potential. Researchers have generated a great deal of interest in this oxide. The structure characteristics phase change mechanism and synthesis preparation and practical application have been extensively studied, it has become a hot topic in the field of functional materials [7]. However vanadium dioxide cannot be manufactured in large quantities due to the harsh preparation conditions and the complicated experimental environment. This feature [8] severely restricts the promotion and application of this new material with excellent performance. The most common methods [9] for preparing vanadium dioxide are magnetron sputtering and inorganic sol-gel methods. Magnetron sputtering method is not suitable for large-scale production because of the harsh experimental conditions and the inorganic sol-gel method. Due to the poor crystallinity and the purity is not high and it cannot be used in industrial manufacturing. The actual vacuum annealing in the tube furnace is 60 Pa to 100 Pa, the control parameters of the two processes of magnetron sputtering [10] and vacuum annealing are optimized to realize the preparation of highly reproducible VO$_2$ thin films [11]. Different experimental conditions were used to study the effects of annealing temperature and annealing time on the composition of the thin films [12], the morphology of vanadium oxide thin films formed under different experimental conditions was studied, which laid the foundation for the production of vanadium dioxide in batches.
2. Experimental process
In experiments, $\text{V}_X\text{O}_Y$ thin films were prepared by magnetron sputtering and vacuum annealing. The specific experimental procedure was as follows: a pure vanadium thin film was prepared using a magnetron sputtering coating machine, and a uniform surface thickness was obtained by oxidizing a pure vanadium substrate in a tube furnace. Oxidation of vanadium dioxide film which taking vanadium pentoxide thin film under different annealing process annealing treatment, in-depth study of different annealing process on $\text{V}_X\text{O}_Y$ thin film crystal morphology and composition of the impact.

2.1. Cleaning of substrates
The substrate was ultrasonicated in a mixed solution of absolute ethanol and acetone for 1 hour, and the solution was prepared in a ratio of 4:1. The solution was then placed in a mixed solution of concentrated sulfuric acid and hydrogen peroxide in a ratio of 2:1. Control the temperature of the water bath heated to 90°C for 1 hour. Rinse the substrate heated in the water bath with deionized water.

2.2. Preparation of pure vanadium thin films
Using a magnetron sputter coater to sputter on a cleaned substrate using a DC pure vanadium target, the reactive gas is high purity argon, chamber pressure 1Pa, chamber temperature 400°C, sputtering power 180W, presputtering 15min then sputtering time 120min.

2.3. Preparation of $\text{V}_2\text{O}_5$ thin films
Use tube furnace to oxidize pure vanadium film in pure oxygen atmosphere, use high purity oxygen to wash gas in tube furnace quartz glass tube for 10min, connect exhaust pipe to deionized water for water blocking, heat to 550°C to close exhaust pipe, The pure vanadium oxide film was oxidized in a pure oxygen atmosphere for 300 min. The $\text{V}_2\text{O}_5$ thin film after oxidation was yellow and the surface was uniform.

2.4. Vacuum annealing
Vacuum annealing is a key step in the preparation of vanadium dioxide. Annealing is performed in a tube furnace with a vacuum of 60 Pa to 100 Pa. this article controls the annealing temperature and annealing time of the sample under the condition that the previous process is unchanged. The purpose is to reveal the effect of annealing temperature and annealing time on the surface morphology and grain growth of the film.

3. Test results and analysis
The $\text{V}_2\text{O}_5$ thin films were annealed at different annealing temperatures and annealing times. XRD and SEM measurements were performed on the thin films under different process conditions. The surface of the morphology composition and grain size of the $\text{V}_X\text{O}_Y$ thin films were investigated at different annealing temperatures and annealing times.

3.1. Effects of Different Annealing Temperatures on Surface Morphology and Product of Thin Films
The annealing time was set to 110 min. The effects of different annealing temperatures on the morphology were observed. The samples were characterized and analyzed.
Figure 1 shows that the surface of the V$_X$O$_Y$ film crystallizes better and gets worse as the annealing temperature increases. The crystal structure of the whole surface is poor when the annealing temperature is 450 °C, the crystal grains are scattered no connection, small crystal grains begin to aggregate together at the annealing temperature of 475 °C; the crystal surface is very uniformity when the annealing temperature reaches 500 °C which shows the best degree of crystallinity; the surface of the crystal begins to become uneven and the overall morphology begins to deteriorate as the temperature continues to rise when the annealing temperature is 520°C.

In order to further understand the thin film product and the crystal structure of the material was characterized using X-ray diffraction, the XRD characterization of the V$_X$O$_Y$ thin film under different annealing conditions temperature was observed.

Figure 2. XRD patterns of films at different annealing temperatures.
The VₓOᵧ films were characterized by XRD at different annealing temperatures by comparison with the PDF#31-1438 card, for ease of observation we shows a diffraction pattern of 18° to 32° extracted as in Figure 2. The result shows that the fixed annealing time is 110 min. Under different annealing temperatures the VₓOᵧ thin film annealing produces that the series of vanadium oxides with different valence states show that when the annealing temperature is 450°C, only a strong diffraction peak of V₂O₅ orientation (001) is detected; the orientation of the film still appears at 20.3° the (001) V₂O₅ diffraction peak when the annealing temperature is 475°C but the diffraction intensity becomes significantly lower.

The V₂O₅ diffraction peak with (110) orientation appears at 26.1° the diffraction peak with V₆O₁₃ orientation (003) appears at 26.9°, the V₂O₅ film begins to decompose indicating that the film has been begin to deoxygenation; with the further increase of the experimental temperature, a strong diffraction peak with VO₂ orientation (011) appears at 27.9° at 500°C, and at 27.9° when the annealing temperature rises to 525°C. The diffraction peak begins to decay slightly. This shows that this temperature has reached the critical upper limit of VO₂ growth, if it continues to increase temperature is not suitable for VO₂ growth. The results show that with the increase of annealing temperature, the crystal orientation of V₂O₅ achieves a transition from V₂O₅ (001) to V₆O₁₃ orientation (003) to VO₂ orientation (011), this temperature has reached the critical upper limit of VO₂ growth because with the increasing of the temperature VO₂ orientation intensity of the (011) diffraction peak becomes lower. The optimum annealing temperature should be between 475°C and 525°C.

3.2. *The Effect of different annealing time on annealing result is studied.*

The annealing temperature is set to 400°C, the tube furnace vacuum degree is 60 Pa to 100Pa, the annealing time is 70min, 110min, 150min and the annealing time on the film material The substrate for the experiment is Al₂O₃ corundum substrate, the crystal structure of the X-ray diffraction instrument, MSAL XD-3 for the diffractometer, and the following image is the XRD diffract graph of VₓOᵧ samples.

![Figure3. Film XRD at different annealing times](image)

Found by comparing the PDF card, at the diffractive angle is 20. 26° A strong V₂O₅ (001) diffraction peak, with the increase of annealing time, the V₂O₅ (001) diffraction peak intensity is lower, indicating that the film component in the (001) orientation of V₂O₅ less and less, with the corresponding in the diffraction angle is 41. The diffraction peak of V₂O₅(002) appeared at 25° and the intensity of the diffraction peak increased with the increase of annealing time, which indicated that the orientation of the film component was V₂O₅ More and more, when the annealing temperature at 400 °C, with the increase of annealing time, the V₂O₅ of the film gradually changed from (001) to (002).
4. Summary
In this paper, a new experimental method was used to fabricate V_xO_y thin films on Al_2O_3 ceramic substrates by combining magnetron sputtering and vacuum annealing processes to achieve the preparation of highly reproducible VO_2 thin films, and to further study the different annealing temperatures for thin films. The surface morphology and the effect of the film product the effect of different annealing times on the cell growth and crystal orientation. The main conclusions are as follows:

(1) In order to generate VO_2 thin film with good phase change performance the annealing temperature should not lower than 475°C while can not exceed 520°C. The lower temperature will lead to under-reduction and too high temperature will lead to over-reduction.

(2) As the annealing temperature increases the crystal grains on the surface of the crystal gradually converge at 500°C to 520°C. The crystal growth rate is faster at 400°C to 500°C but the nucleation rate is slower. The nuclear rate gradually becomes faster and large groups begin to form. The size of the crystallites grows longer with the increase of the annealing time and reaches the optimal value at about 110min.

(3) The vanadium oxide manufacturing method which combines the magnetron sputtering method and the vacuum annealing process optimizes the control parameters of the two processes of magnetron sputtering and vacuum annealing process, it solves the problem that the magnetron sputtering reproducibility is not the good drawbacks avoid the disadvantages of poor crystallization of the sol-gel method, uneven surface of the film with the low purity it also reduce the experimental requirements for the accuracy of the experimental apparatus a large-grained VO_2 thin film is prepared. The experiment has a guiding role in further studying the large-scale production of VO_2 thin film.

5. References
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