Preparation of Vanadium Dioxide Thin Films with Adjustable Electric Field Intensity Transition Point

Shi-Hao SHAN[1,a *], Qing-Guo WANG[1,b], Zhao-Ming QU[1,c], Wei CHEN[1] and Ang LI [1]

[1]Institute of Electrostatic & Electromagnetic Protection, Ordnance Engineering College, Shijiazhuang 050003

[a]13032632585@163.com, [b]qingguowang99@aliyun.com, [c]iamqzm3990@163.com,

*Shan Shihao

Keywords: Inorganic sol-gel method, vacuum annealing, electric field strength phase change point adjustable, vanadium dioxide thin film

Abstract. Preparation of phase change electric field adjustable vanadium dioxide thin films on Al_2O_3 ceramic substrates by inorganic sol - gel method and vacuum annealing process. By changing the annealing process to adjust the proportion of vanadium dioxide in the film to achieve changes in its phase change electric field threshold. And It had been found that the electric field intensity transformation point was reduced from 1.8MV/M to 0.4 MV/M and Phase change electric field strength decreased by about 4 times. It has also been found that the resistance abrupt multiplier decreased as the field phase change point decreased and the change range of the phase change was $2 \times 10^3 \sim 1 \times 10^2$.

Introduction

Vanadium dioxide can be reversibly changed from monoclinic structure to tetragonal rutile structure at near room temperature (about 68 °C) [1], and its optical, magnetic, electrical properties have also mutated with the crystal structure. This excellent optical electromagnetism makes VO_2 a great potential in smart windows [4], electrical switches [5], terahertz devices [6].

With the continuous research of vanadium dioxide in recent years, the control technology of vanadium dioxide phase transition temperature has been basically mature, mainly in the following three ways: adjust the applied stress[8-9], control the microstructure[10-12] and ion doping[13-15]. But the control of the phase change field strength was basically not studied, There were two main reasons for this. On the one hand, most of the applications of vanadium dioxide were mainly based on the theoretical basis of the thermo-phase transition of vanadium dioxide. On the other hand, the effect of ion doping on the transformation field of vanadium dioxide was not obvious. In this way, the successful development of a preparation of vanadium dioxide film adjustable phase change electric field technology was very meaningful.

The regulation of the phase change electric field can also be divided into three methods: regulating the external stress, controlling the microstructure and ion doping. However, due to ion doping on the vanadium dioxide electric field threshold control was not obvious, so the control of micro-morphology was preferred. For the control of micro-morphology can be also divided into the following categories: control the film's compactness, control the size of grain and control the content of VO_2. For the electrical performance, the film should have a high density. In the case of grain size, the size of the grains could change the phase transition point of the electric field, the principle was similar to that of the ZnO nano-particles, but it was difficult to prepare by using sol-gel. In contrast, the simpler method of controlling the intensity transition point of the electric field was to change the content of VO_2. the amount of V_2O_5 reduced to VO_2 was controlled by using the vacuum annealing process. So that the proportion of controlled VO_2 in the film can be achieved. And so the purpose of controlling the intensity transition point of the vanadium dioxide electric field was realized.

In this paper, VO_2 thin films were prepared by inorganic sol-gel method and vacuum annealing process. The phase change electric field was prepared by changing the vacuum annealing temperature on the Al_2O_3 ceramic substrate. And the temperature phase transition point test and the electric field intensity transformation point test were carried out for each sample. It was found that the phase transition point of vanadium dioxide was reduced from 1.8MV/M to 0.4 MV/M, and the phase transition electric field was reduced by more than 4 times. It was also found that with the decrease of phase transition point of electric field intensity, the resistance abrupt multiplier was reduced ($2 \times 10^3 \sim 1 \times 10^2$).

Experimental Process

Preparation of VO2 Thin Films

Preparation of V2O5 sol

The VO_2 thin films were prepared by inorganic sol-gel method and vacuum annealing process. The specific experimental procedure was as follows: take 5g V_2O_5 (purity 99.9%) in the crucible into the 850 °C muffle furnace for 15min. Take 250 ml of deionized water in a beaker, the beaker placed on a magnetic stirrer, select the speed of 2800 r/min, the molten vanadium pentoxide was rapidly introduced into deionized water, after stirring for one minute, the beaker was placed on a constant temperature stirrer at a temperature of 60 °C for 2 h. At last the solution was allowed to stand for 48 h.

Cleaning of the substrate

The substrate was placed in a mixed solution (8: 2) of anhydrous ethanol and acetone for 1 h, and then placed in concentrated solution (1: 9) of concentrated hydrochloric acid and deionized water for 1 h. Finally rinse off with deionized water.

Pull the coating

The cleaned substrate was placed on the clip of the pull-up coating machine, select the coating parameters: The descending speed is 2000um/s, the standing time in the sol is 100 s and the pulling speed is 2000um / s, after the completion of a pull, the vanadium pentoxide wet film was dried in a 100 °C oven for 15 min and then subjected to a second coating and circulated 4 times. In order to increase its adhesion[16], the coated vanadium pentoxide dried film was dried in a 200 °C oven for 200 min.

Vacuum annealing

Vacuum annealing is the most critical step in the preparation of phase change electric field threshold adjustable vanadium dioxide, where annealing temperature and annealing vacuum are important for V_2O_5 to be fully reduced to VO_2. During the annealing process, the sample is reduced from V_2O_5 to VO_2, which is a process for the precipitation of oxygen. If the annealing temperature is low enough, when a part of the sample V_2O_5 converted to VO_2, the precipitation of oxygen in the annealing furnace will reduce the vacuum, and thus fail to restore the conditions of VO_2, V_2O_5 can only be reduced to V_6O_{13}. So the level of control of the annealing temperature can be indirectly controlled V_2O_5 converted to the amount of VO_2, and thus control the content of VO_2 in the film. The specific implementation process was as follows: three samples were annealed at 480 °C, 500 °C and 520°C, respectively, the annealing time was 8 h, heating and cooling rate was 11°C/min and the vacuum was 50 Pa to 100 Pa.

Test Methods

Two different methods were used to test the temperature transition point and the electric field strength change point of the material.

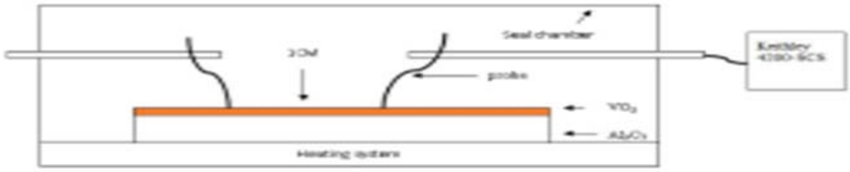


Fig1.Temperature phase change point test schematic

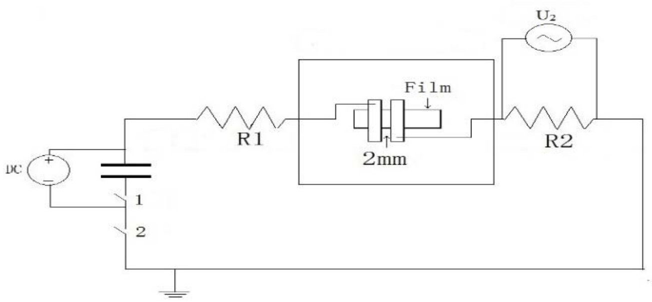


Fig 2. electric field strength phase change point test system schematic diagram

Three temperature samples were tested using a two-probe test system, specific test chart shown in Figure 1. Two probe spacing 1CM, and the bottom of the substrate was the temperature control system, the accuracy of temperature was 0.5 °C. In order to ensure the sensitivity of the temperature test system to temperature, the whole system was sealed in a heat preservation chamber and insulated from the outside. Finally Keithley 4200-SCS was used to collect test data.

The high voltage test system was used to test the phase transition point of the electric field, specific test chart was showed in Figure 2. A large capacitor was used as a voltage source, this was mainly because on the one hand large capacitors was used to avoid damage to high voltage sources, on the other hand in high pressure environment, high voltage output was instability. During the test,fist turn off the switch 1 and turn on the switch 2 to charge the capacitor, and then turn on the switch and turn off the switch 2 to test the material. Moreover current limiting resistor R_1 resistance was 30 MΩ, and the sampling resistor R_2 resistance was 1000 Ω. In addition the fixture was made of copper electrode, the size was 10mm × 10mm × 50mm, the distance between the two fixtures was 2mm. Furthermore the two electrodes in contact with the surface of the material, the rest were made all over the chamfer, to avoid cutting-edge discharge, at the same time, in order to avoid flashover due to high voltage flash [17], fill in the temperature control system SF_6. The sample resistance was measured by the DC output voltage U_0 and the oscilloscope voltage U_2 calculated by Equation 1, and the phase change electric field was calculated by Equation 2

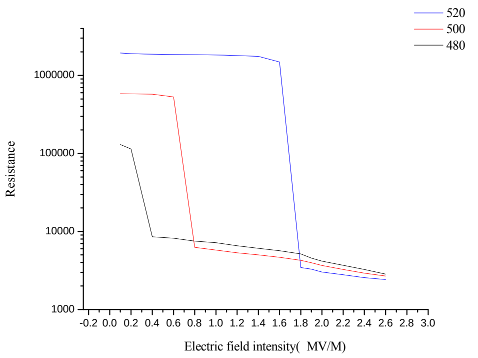
$$\frac{1}{R}=\frac{U_2}{U_0R_2-U_2R_1-U_2R_2} \tag{1}$$

$$E_T=\frac{V_T}{d} \tag{2}$$

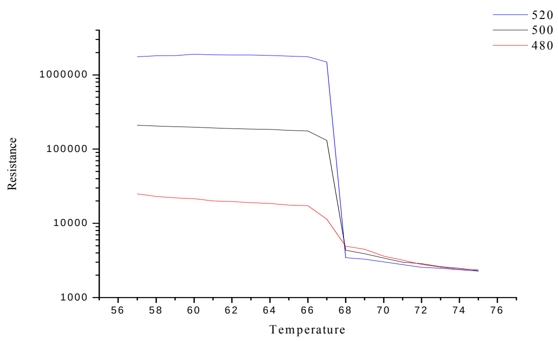
Test Results and Analysis

Fig.3(a) showed the relationship between the temperature transition point at different annealing temperatures. It was also showed that as the annealing temperature decreases, the resistance decreases at room temperature. For example, when the vacuum annealing temperature was 520 °C, the resistance at room temperature was 10 MΩ, when the vacuum annealing temperature was

500 °C, the resistance at room temperature was 0.6 MΩ, and when the vacuum annealing temperature was 480 °C, the resistance at room temperature was 0.6 MΩ, The main reason for this phenomenon was the lower the annealing temperature, the less the content of VO_2 in the film, and another reason was other valence of the vanadium oxide resistance was lower than VO_2 at room temperature. At the same time, we also found that the temperature transition point of the three samples did not change, indicating that this method does not affect the material phase transition temperature, but would change the material before and after the transformation of the resistance value.



(a)



(b)

Fig 3 Temperature (a) and electric field strength (b) transformation point test chart

Figure 3 (b) shows the relationship between the phase transition point of the electric field at different annealing temperatures. It could be seen from Figure 3 (b) with the annealing temperature decreases, the electric field intensity transition point was also constantly reduced. When the annealing temperature was 520 °C, the electric field intensity transition point was 1.8MV/M, when the annealing temperature was 500 °C, the electric field intensity transition point was 0.8MV/M and when the annealing temperature was 480 °C, the electric field intensity transition point was 0.4 MV/M. But at the same time we also found that with the VO_2 thin film electric field strength transformation point of the reduction, the phase change factor also decreased. For example, When the annealing temperature was 500 °C, the resistance change was 3×10^2 times and when the annealing temperature was 480 °C, the resistance change was 1×10^2 times. The main reason for this phenomenon was that the reduction of the electric field intensity transition point was achieved by reducing the content of VO_2 in the film, the lower the content of VO_2 in the film, the less energy it needed to excite the electric field. However, with the decrease of VO_2 content in the film, the phenomenon of phase change was less obvious because the vanadium oxide containing more valence in the film reduced the resistance value of the film at room temperature. So the phase transition factor decreased as the phase transition point of the electric field decreased. The Fig 3 (b) also showed that by using this method of preparation reduced the intensity transition point of the VO_2 for electric field was below 1MV/M, about 0.4 MV/M, which was reduced more than 4 times.

Conclusion

In this paper, three samples with annealing temperature of 520 °C, 500 °C and 480 °C were prepared on the Al_2O_3 ceramic substrate by using inorganic sol-gel and vacuum annealing, and the temperature transformation point test and the electric field intensity transformation point test were carried out for the three samples respectively. It was found that the vanadium dioxide thin film prepared by using this method did not affect the phase transition temperature, and all the phase transition temperature of the three samples were 68 °C, but it would affect the phase change factor ($2 \times 10^3 \sim 1 \times 10^2$). At the same time, the phase transition point of the electric field intensity of the three samples showed a significant change. It was found that the phase transition point of the electric field decreased from 1.8MV/M to 0.4MV/M with the decrease of annealing temperature. In this experiment, it was proved that the phase transition point of the electric field could be adjusted, and the phase transition point of the VO_2 electric field was reduced to less than 1 MV/M, about 0.4 MV/M, and the field strength was reduced About 4 times by using this method. In summary, it was of great significance to extend the application range of vanadium dioxide by using this method.

Reference

[1] Morin F J. Oxides which show a metal –to-insulator transition at the Neel temperature, J. Phy. Rev. Lett. 3(1) (1959) 34-36.

[2] Xiong Ying, Wen Qi, Tian Wei, Mao Qi, Chen Zhi, Yang Qinghui, Jing Yulan.Study on electrical properties of silicon-based vanadium dioxide transition film, J. Acta Physica Sinica. 64 (1) (2015) 017102

[3] Ruzmetov D, Zawilski K T, Narayanamurti V, et al. Structure-functional property relationships in rf-sputtered vanadium dioxide thin films, J. Journal of Applied Physics. 102(11) (2007) 113715 - 113715-7.

[4] Huang Zhangli, Chen Sihai, LU Chaohong,et al. Infrared characteristices of VO_2 thin film for smart window and laser protection applications, J. Applied Physics Letters. 101 (19) (2012) 191905.

[5] Stefanovich G, Pergament A, Stefanovich D. Electrical switching and Mott transition in VO2, J. Journal of Physics Condensed Matter. 12(41) (2000) 8837.

[6] Qiu D H, Wen Q Y, Yang Q H, et al. Growth of vanadium dioxide thin films on Pt metal film and the electrically-driven metal–insulator transition charact-eristics of them, J. Acta Physica Sinica Chinese Edition. 62(21) (2013) 217201-590.

[7] Wen Q Y, Zhang H W, Yang Q H, et al. Terahertz metamaterials with VO_2 cut-wires for thermal tunability, J. Applied Physics Letters,. 97(2) (2010) 021111-021111-3.

[8] Y.Muraoka and Z. Hiroi, Metal–insulator transition of VO2 thin films grown on TiO2 (001) and (110) substrates, J. Appl Phys Lett. 80 (2002) 583-585.

[9] F. C. Case, Modifications in the phase transition properties of predeposited VO_2 films, J. Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films. 2 (1984) 1509-1512.

[10] M. B. Sahana, M. S. Dharmaprakash and S. A. Shivashankar, Advances in thermochromic vanadium dioxide films, J. Mater chem. 12 (2002) 333-338.

[11] Luo Y Y, Zhu L Q, Zhang Y X, et al. Optimization of microstructure and optical properties of VO_2 thin film prepared by reactive sputtering, J. Journal of Applied Physics. 113(18) (2013) 1191.

[12] Whittaker L, Jaye C, Fu Z, et al. Depressed phase transition in solution-grown VO_2 nanostructures, J. Journal of the American Chemical Society. 131(25) (2009) 8884.

[13] Tan X, Yao T, Long R, et al. Unraveling Metal-insulator Transition Mechanism of VO_2 Triggered by Tungsten Doping, J. Scientific Reports. 2(6) (2012) 466.

[14] Whittaker L, Wu T L, Patridge C J, et al. Distinctive finite size effects on the phase diagram and metal-insulator transitions of tungsten-doped vanadium(IV) oxide, J. Journal of Materials Chemistry. 21(15) (2011) 5580-5592.

[15] Patridge C J, Whittaker L, Ravel B, et al. Elucidating the Influence of Local Structure Perturbations on the Metal–Insulator Transitions of V_1–xMoxO_2 Nanowires: Mechanistic Insights from an X-ray Absorption Spectroscopy Study, J. Journal of Physical Chemistry C. 116(5) (2012) 3728-3736.

[16] Chae B G, Kim H T, Yun S J, et al. Highly oriented VO_2 thin films prepared by sol-gel deposition method, J. Electrochemical and Solid-State Letters. 9(1) (2005) C12-C14.

[17] Wang Caixiong,Tang Zhiguo,Chang Wenzhi,et al. Experimental Study on Development Characteristics of Point Discharge in GIS , J. Power System Technology . 35(11) (2011) 157-162.