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Influence of temperature on the electro-induced MIT of VO_2 prepared by the magnetron sputtering method

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ABSTRACT

Vanadium dioxide (VO_2) is a typical representative of the strongly correlated electronic system. It presents a reversible first-order metal-insulator transition once stimulated by temperature, voltage, light, or pressure. The insulation-metal phase transition (MIT) makes it a new type of functional material with excellent potential applications in many fields. In this paper, magnetron sputtering technology and the "two-step method" process are used to prepare the VO_2 films with phase transition properties. The results show that after the classic V film is processed for more than 100 minutes in air, and annealed in N_2 atmosphere for 150 minutes, the VO_2 (M) can be obtained with a resistance change rate more than three orders of magnitude. The study of the resistance change under the action of temperature and voltage found that the temperature of the heating and cooling phase transition are 67.4℃ and 62.8℃ respectively, and the hysteresis width is 4.6℃. The relationship between phase transition voltage and ambient temperature is presented based on the heat dissipation model. It is found that Joule heating plays a significant role in the electro-induced phase transition of VO_2. Furthermore, the ambient temperature has an obvious regulation effect on the phase transition voltage of VO_2 film. The research results can provide efficient guidance to the preparation of VO_2 film and the application and regulation of electro-induced phase transition.

Keywords: Vanadium Dioxide, Magnetron Sputtering, Electro-induced Phase Transition, Joule Heating

1. INTRODUCTION

Vanadium dioxide (VO_2) is a metal oxide with insulation-metal phase transition (MIT) [1]. Under the stimulation of external conditions such as heating [2], pressure [3], light [4], the reversible transformation from the insulating state of the monoclinic rutile structure to the metallic state of the tetragonal rutile structure can be completed in a short time [5]. The transition process is accompanied by sudden changes in physical properties such as electrical conductivity [6] and light transmittance [7]. It has shown great application potential in the fields of smart windows [8], reconfigurable antennas [9], terahertz radiation [10], and intelligent electromagnetic protective materials [5].

The excellent phase change performance of VO_2 has been verified and preliminarily applied. However, vanadium is an element with polyvalent states such as +2, +3 +2, +3, +4, +5 [11], and a variety of non-stoichiometric compounds [12] in the vanadium-oxygen system. Furthermore, the multiple phases, such as M1, M2, T, R, and B in the VO_2 system, can be mutual-transformed with the pressure of positive voltage and temperature [13]. Therefore, it is quite challenging to prepare the high-pure VO_2. At present, the commonly used methods for preparing VO_2 films include magnetron sputtering [14], molecular beam epitaxy [15], sol-gel method [16], and pulsed laser deposition [17, 18], etc. And their preparation principles and processes are different. Among them, magnetron sputtering technology has great advantages in the preparation of high-quality VO_2 films due to its high consistency and convenient operation.

In terms of the VO_2 thin film, most of the research are focus on the smart windows [19] whose electro-induced phase change performance [20] also has excellent application prospects. However, the research topic is quite emerging, and more research are significantly necessary. In this paper, using magnetron sputtering technology combined with the annealing process, the adjustment technology of VO_2 on Al_2O_3 ceramic substrate preparation process was studied. To be specific, the pure vanadium film was firstly prepared by a

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magnetron sputtering apparatus. Secondly, a high-quality vanadium oxide film was prepared by a two-step method of air oxidation and nitrogen reduction. The control technique and electro-induced phase transition performance of VO_2 thin film were finally studied and discussed.

2. MATERIALS AND METHODS

2.1 Preparation

In the preparation of pure V film by magnetron sputtering, 99.99% purity vanadium target is used as a sputtering target. Moreover, 99.99% purity Ar is used as an ionizing working gas. The sputtering temperature is 250℃, and the power supply is 200 W. The vacuum degree is less than 10^{-4} Pa and the working pressure is maintained at 1 Pa. A pre-sputtering is carried out for 10 minutes before each experiment to liminate the adverse effects of pollution caused by the oxides and impurities. The thickness of the V film is adjusted by changing the sputtering time. The Step profiler (Bruker Countor GT K &, KLA-Tencor D120) is used to test the thickness of the sample. The thickness of the sample is about 100 nm when a sputtering time lasts 30 minutes.

V_2O_5 is a substance with the highest valence and the most stable properties in the vanadium-oxygen system. Compared with the direct preparation of VO_2, the technical route where V_2O_5 is firstly obtained and then reduced has low equipment requirements and a wider time window. In this paper, air was used as the reaction gas to perform oxidation in a tube furnace to reduce the experimental requirements. However, the over-long time oxidation process can cause the evaporation of the film and consequently reduce the thickness of the film. The oxidation time can be optimized by studying the morphology and crystal phase of the V_2O_5 film with different oxidation time.

Once the V_2O_5 film is ready, the reduction is the crucial step to determine the phase change performance of the film. The reduction process of V_2O_5 is V_2O_5-V_6O_{13}-V_6O_{11}-VO_2-V_2O_3, which is usually a process of oxygen evolution [21]. The reaction process is together with a series of complex reactions such as reduction reaction and disproportionation reaction, which are more sensitive to the experimental conditions. Increasing the reaction temperature T and reducing the oxygen partial pressure will assist to precisely process the decomposition reaction [21]. The low oxygen partial pressure environment can be fulfilled by absolute vacuum or relative vacuum. Absolute vacuum needs vacuum equipment which increases the experimental cost. Therefore, this article employed the second method to achieve relative oxygen vacuum: the V_2O_5 film prepared is annealed in a tube furnace at 500℃ and N_2 atmosphere. The charcoal gallic acid solution is used to absorb oxygen and silica gel to remove water vapor to improve the purity of N_2 and reduce the O_2 content of the introduced gas.

2.2 Characterization

Several techniques were used to characterize the as-synthesized films. The XRD patterns were obtained on an X-ray polycrystal diffractometer (XD6, Beijing Puxi General Instrument Co., Ltd.) by using Cu Kα radiation at 36 kV and 20 mA in a 2θ range between 10^o and 90^o with a step of 8^o per minute. The identification of the compound was made by comparing the patterns to the Joint Committee on Powder Diffraction Standards (JCPDS). The morphology and microstructure of VO_2 films were investigated by high-resolution scanning electron microscopy (SEM, Gemini SEM 300 SEM instrument, Germany) under 5 kV. The measured samples were deposited and adhered to carbon tapes and subsequently deposited with a 7 nm thin layer of platinum on the surface to prevent the charging effect. And the D.C. resistivity characterizations respect to temperature and electric field were detected by using a semiconductor parametric analyzer (Keithley 2600). The maximum current is 10 mA in the range of 0-100 V.

In order to study the effect of oxidation time on the V_2O_5 film, the V film prepared by magnetron sputtering was oxidized at high temperature in air for 100 minutes, 200 minutes and 300 minutes, respectively. The XRD patterns of the sample obtained by oxidation are shown in Figure 1. It can be seen from the figure that in the sample without annealing (0 min), the diffraction peaks of the substrate A_2O_3 appear only. The phenomenon is because that the V thin film prepared by magnetron sputtering at room temperature is amorphous. By comparing with the V_2O_5 standard card (JCPDSPDF#72-0433), the V_2O_5 peak appears when the V film is oxidized in the air for 100 minutes. The diffraction peaks (010) and (110) of V_2O_5 are enhanced with the increase of oxidation time, while the increase characteristics no more appear when the oxidation time is increased to 300 minutes. The film prepared by magnetron sputtering evaporates at high temperature, leading to a thinner film with unexpected performance. This article chooses the oxidation time of 200 minutes.

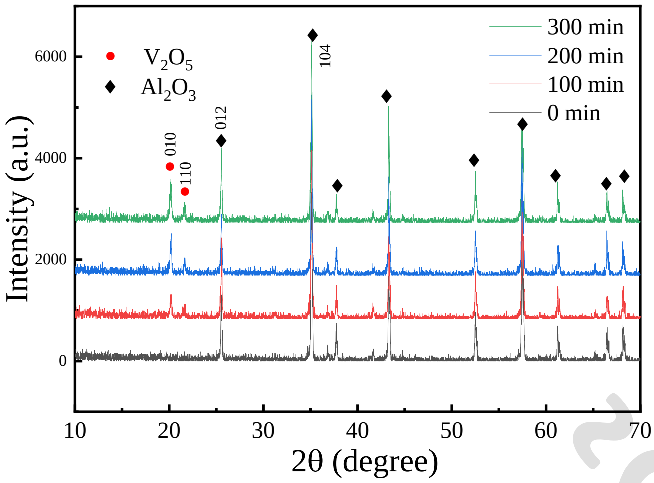

Figure 1: XRD patterns of samples with different oxidation times

The prepared V_2O_5 samples were characterized by SEM to observe the micromorphology as shown in Figure 2. The prepared V film has a layered structure. After 100 minutes of annealing, small crystals appeared (Figure 2b) with a particle size of about 200 nm. When the annealing time was increased to 200 minutes (Figure 2c), the crystals appeared to be layered. As the annealing time increases further, the grain size increases and the particle size consistency improves. The maximum particle size is about 800 nm. The process of preparing V_2O_5 by oxidizing the pure V thin film is that amorphous V element first generates small V_2O_5 particles under the action of high temperature and oxygen. As the oxidation time increases, the small particles keep fusing, and the particle size increases. The MIT behaviour of VO_2 (M) is highly related to the grain size and the potential energy of the crystal phase [22]. Therefore, by changing the oxidation time, both the crystal grain size and the phase transition critical performance of the film can be adjusted.

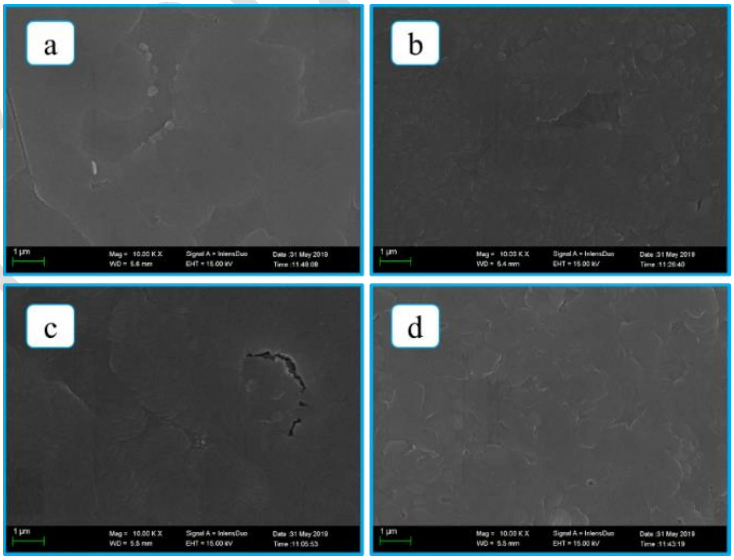

Figure 2: SEM images of samples with different oxidation times. (a) V film, (b) the oxidation time is 100 min, (c) the oxidation time is 200 min, (d) the oxidation time is 300 min.

The V_2O_5 film with a 200 minutes oxidation was annealed in N_2 atmosphere at 500°C to obtain VO_2 (M) with MIT properties. After processed with different annealing times, four sets of different samples were obtained. The XRD curves of the samples are shown in figure 3. The diffraction peaks of the sample without annealing correspond to V_2O_5. After the annealing process for 30 minutes, the V_2O_5 phase disappears, but new phase is no more generated in this time. After annealing for 60 minutes, theV_6O_{13} diffraction peaks appear in the pattern. When the annealing time reaches 100 minutes, the VO_2 (M) peak appears. It shows that the V_2O_5 film with a thickness of about 100 nm is treated with N_2, the minimum annealing time at 500℃ is 100 minutes.

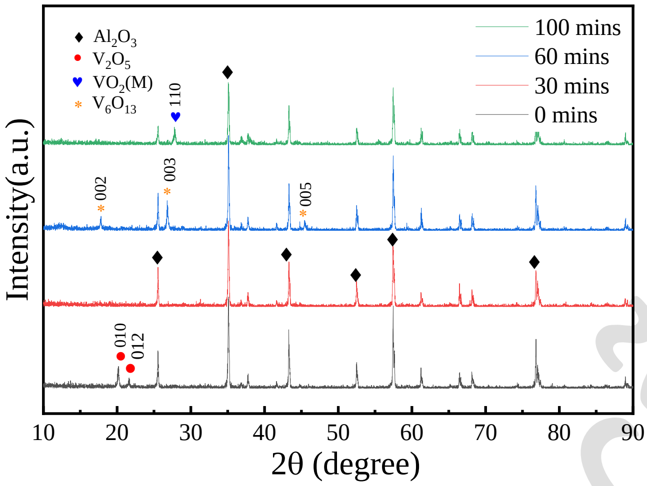

Figure 3: XRD patterns of samples with different annealing times

3. RESULTS AND DISCUSSION

The MIT behaviour of VO_2 is the most important feature. Pure-silver electrodes are sputtered on the film surface (figure 4) to study its phase transition characteristics, which can protect the sample, and improve the repeatability of the experiment. The space of the electrode is 0.4 mm, and the width is 0.5 mm.

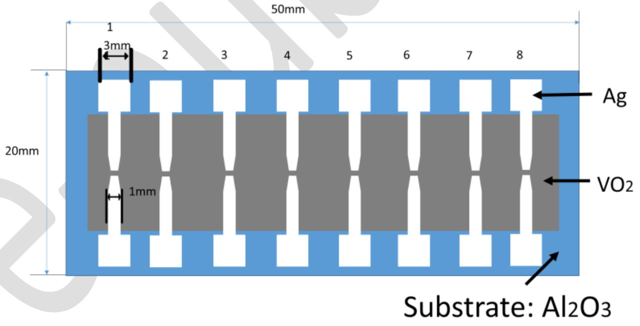

Figure 4: Schematic diagram of the silver electrode on the surface of VO_2 film

The temperature-induced MIT test is carried out in a thermostat. A resistance tester is used to test the resistance change between the electrodes, and the temperature probe of the resistivity tester is used to monitor the surface temperature of the film. The phase transition temperature T_c is usually defined as the temperature at the extreme value of the differential curve of heating and cooling [23]. As shown in Figure 5, the resistance of the thin film resistor changes in the heating and cooling process. The resistance changes from 60 kΩ at room temperature to 8 Ω at 90°C. The resistance change rate exceeds three orders of magnitude. In Figure 5b, the phase transition temperature T_c during the heating and cooling process is 67.4°C and 62.8°C, and the hysteresis temperature is 4.6°C. It shows that the VO_2 film with high phase transition coefficient was successfully prepared.

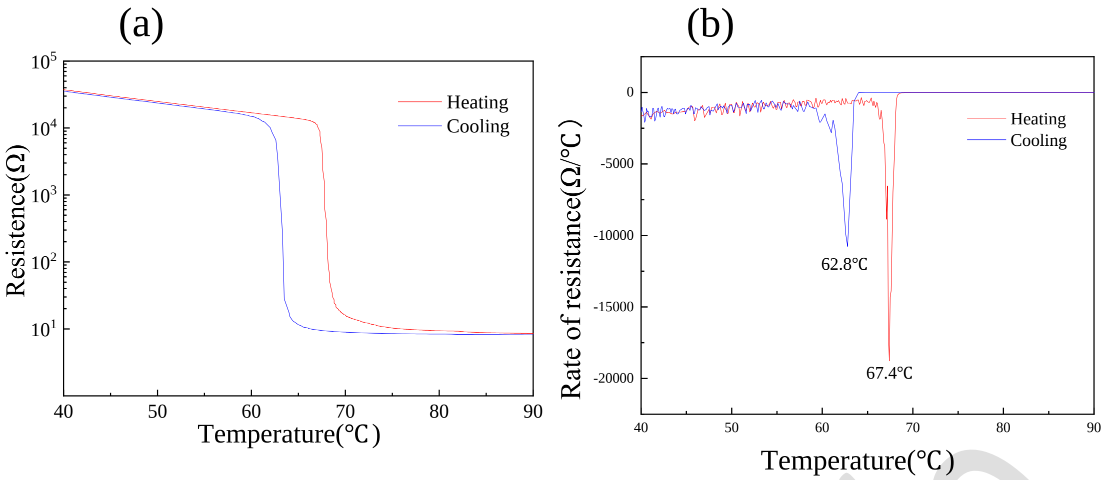

Figure 5: (a) Temperature-induced phase transition curve (b) the slope of the temperature-resistivity curve (the red lines are the healing process, the blue lines are the cooling process)

Like the phase transition property with temperature, the VO_2 film also present a sharp change in resistance with voltage. [24]. The electro-induced phase transition (e-MIT) has the advantages of fast response speed, a more convenient mode of action. It is more conducive to the miniaturization and intelligent application of devices. Figure 6 shows a repeated *V-I* test for the sample. The phase transition voltage V_c of the sample is about 40 V, and the field strength is 100 kV/m, which is slightly smaller than the the result in [25]. The reason is that the single-crystal nanowires were used as the test object in [25], while the samples in this paper are polycrystalline film. The inevitable defects and impurities in the preparation process can reduce the resistance and V_c of the sample. However, the prepared samples have excellent repeatability, and the consistency is high as shown in Figure 6.

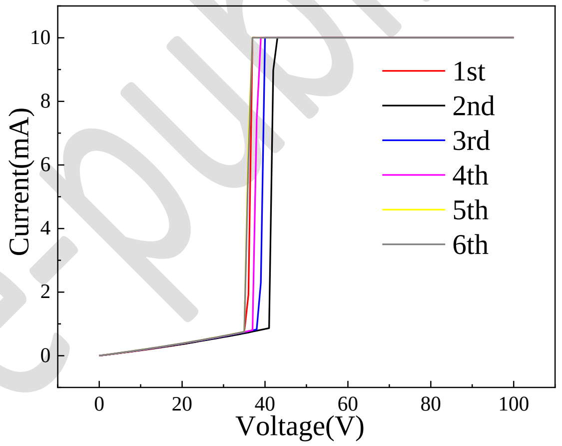

Figure 6: Repeated voltage test curves of the sample

The e-MIT performance of VO_2 is also related to the external temperature, pressure and doping [26]. The critical MIT voltages were tested at different external temperatures (Figure 7) to study the effect of temperature on V_c of VO_2 samples. When the temperature is 62.5°C, the MIT voltage is very close to V_c at room temperature. When the temperature is higher than 68°C, phase transition no more occurs. The MIT voltage of the material changes with the external temperature, as shown in Figure 8. The e-MIT voltage of the film decreases with the increasing temperature.

It is known that Joule heat plays a significant role in the e-MIT [27]. This verification was obtained through electrothermal simulation, Fourier conduction equation calculations, and different experimental results. The calculated DC I-V characteristics and the incubation time showed good agreement with the measured values. Furthermore, some studies revealed that the conductive channel has a greater influence on the electro-induced phase transition. The material phase transition is because of the local temperature in VO_2

reaching the phase transition temperature. According to the thermal balance formula, the total energy in the material is related to the heat generated by Joule heat and the temperature increase of the material. When a phase change occurs, the material can reach equilibrium. So, the relationship between the phase change voltage of VO_2 and the temperature is $V \propto (1-T/T_c)^2$ [28], where V is the MIT voltage when the external temperature is T, and T_c is the MIT temperature. According to the above analysis, T_c is 67.4℃. Suppose $V=k(1-T/T_c)^2$. When T is 62.5℃, the phase change voltage is 44 V, and the coefficient k is 6619.28. The relationship between the MIT voltage V and the external temperature T is shown as the red curve in Figure 8. It is clear that the fitted curve is highly consistent with the test data.

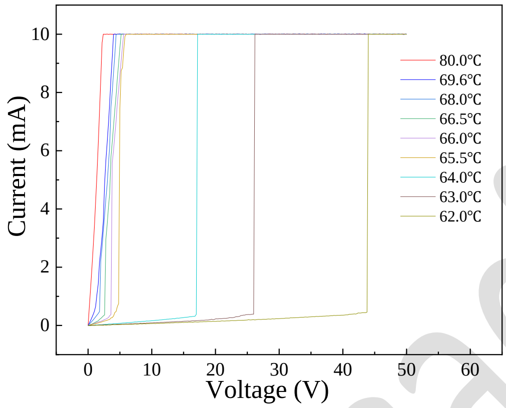

Figure 7: The e-MIT curves at different temperatures

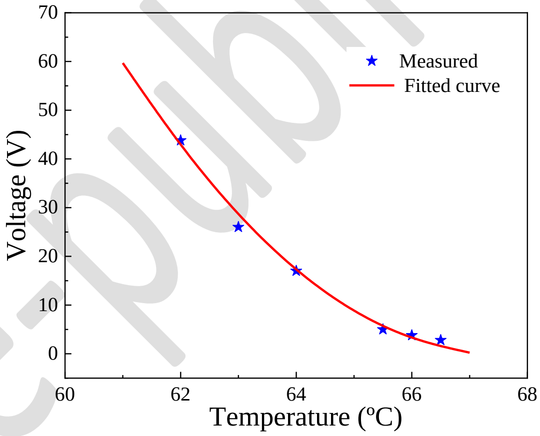

Figure 8: Curve of temperature and phase change voltage

4. CONCLUSION

In this paper, based on the magnetron sputtering technology and atmospheric annealing process, VO_2 polycrystalline film were successfully prepared on Al_2O_3 ceramic substrate. The resistance change rate is higher than three orders of magnitude. And its phase transition characteristics were also studied. The results show that when the oxidation time is more than 100 minutes, a V_2O_5 film with uniform particles and morphology can be obtained. However, the over-long oxidation time can reduce the thickness of the film. The intermediate products V_6O_{13} can appear in the process of reducing V_2O_5 in an N_2 atmosphere. When the annealing time is more than 100 minutes, VO_2 (M) is prepared. The phase transition performance test shows that the resistance of the VO_2 (M) samples present obvious drifts under the action of temperature and voltage. The phase transition temperatures for heating and cooling are 67.4℃ and 62.8℃, respectively. The hysteresis temperature is 4.6℃. The electric field strength at room temperature is 100 kV/m. The relationship between the MIT voltage and the ambient temperature is also obtained. The research results can assist to select the proper annealing conditions for VO_2 films prepared by magnetron sputtering. The results of the phase transition temperature and phase transition voltage and their relationship could provide guidance for designing the threshold switch devices and sensors based on VO_2.

5. FUNDING

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