VO_x films prepared by DC magnetron sputtering

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VO_x films fabricated by direct currect (DC) magnetron sputtering using a high pure vanadium metal target (99.99%) are reported. The impact of the temperature coefficient of resistance (TCR), the effects of Ar/O_2 ratio on the deposition, the sputtering power, the gas pressure, and the annealing temperature and time are analyzed through the design of an orthogonal experiment. The result shows that VO_x films prepared by this method have a relatively high TCR. The the annealing temperature and time of the VO_x films are studied using the RTP-500. The relationships between TCR and annealing temperature and time are obtained. It illustrates that rapid annealing results in an optimized TCR in the range from –2%/K to –3.6%/K.

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VO_x has attracted much attention due to its characteristically good electrical-to-optical transition and thermal sensitivity. VO_x has more than 20 varieties, including VO, V_2O_3, VO_2, V_3O_5, V_6O_{11}, V_4O_9, and V_2O_5. Its semiconductor-to-metal transition at about 68 °C is accompanied by a crystallographic transition from a low-temperature monoclinic phase to a high-temperature tetragonal retile structure. This phase transition is associated with abrupt changes in the optical and electrical properties. Therefore, VO_2 has many potential applications in thermal-optical switches and thermochromic smart windows[1−3].

VO_2 films are fabricated by various deposition methods, such as sol-gel process, vacuum evaporation, and reactive magnetron sputtering. The reactive magnetron sputtering method is one of the most promising techniques for depositing a large area of VO_2. However, fabrication of the VO_2 film by this method requires precise control of the oxygen flow[4].

In this experiment, VO_x films were fabricated by direct currect (DC) magnetron sputtering using a high pure vanadium metal target (99.99%). Through the design of an orthogonal experiment, the impact of the temperature coefficient of resistance (TCR), the influences of Ar/O_2 ratio, the sputtering power, the gas pressure ratio, and the annealing temperature and time on TCR of VO_x were analyzed. The results show that VO_x films prepared have a relatively high TCR.

The VO_x films were deposited on silica glass or N(100) silicon substrate. The pressure of the vacuum chamber was evacuated down to 1×10^{-3} Pa. The thickness of the VO_x films was measured by a spectroscopic ellipsometer. The TCR of the VO_x films was measured by the four-point probe method.

The fabrication of the VO_2 film was investigated using the orthogonal experiment. The parameters of the process conditions are listed in Table 1. The orthogonal experiment table of four factors and four levels served as a guide for the experiments, and it enabled the study of the effects of the main factors on the performance of the VO_x films.

Figure 1 shows the relationships between the TCR and the ratio of Ar/O_2, sputtering power, gas pressure, and substrate temperature of VO_x. The TCR is the average TCR value of the orthogonal tested samples.

The proportion of the oxygen pressure to the gas pressure is important. It directly affected the composition of the film and the oxygen vacancy. In Fig. 1(a), when the oxygen content is low, the TCR has a low value. The lower total TCR value is due to the instability of the V-O bond in a film with greater metal composition, and the TCR values of the metal above zero are offset by the negative temperature coefficient resistance. The sputtering

Table 1. Experimental Parameters

Ratio of Ar/O_2	Sputtering Power (W)	Gas Pressure (Pa)	Substrate Temperature (°C)
100:1	70	1	27
100:2	120	2	200
100:3	150	3	300
100:4	180	4	400

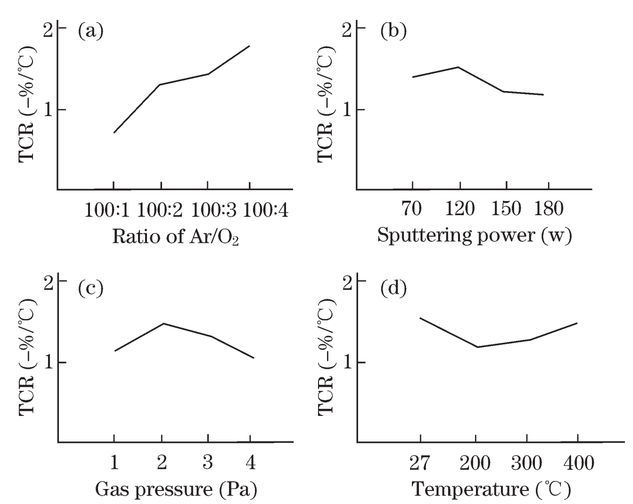

Fig. 1. Relationships between TCR and (a) ratio of Ar/O_2, (b) sputtering power, (c) gas pressure, and (d) substrate temperature.

power determined the energy of the incident particles and affected the components of thin films. In Fig. 1(b), when the power is 70 W, the VO_x films containe many components of V_2O_5, and resistance is significant and unstable. When the power is 180 W, the VO_x films containe more metal composition. A power of 120 W is observed to be appropriate. The gas pressure influences the denseness of the thin films, crystalline state, and TCR value. Figure 1(c) shows that when the gas pressure is low, the generated plasma density is very low. In a short time, it became difficult to form sequent thin films. The highest curve shows the best gas pressure. In Fig. 1(d), it can be seen that the deposition temperature had a certain influence on TCR. When the deposition temperature is 300 °C, the thin film adheres to the substrate, and has a large mechanical strength. At the same time, the increase of crystallization of the grain and decrease of grain boundary density were directly proportional to the increase of the TCR of the thin films. According to research and experiments, optimized preparation parameters were gained. The optimum ratio of Ar/O_2 is 100:4, and the optimum power is 120 W. The best substrate temperature and pressure of work are 300 °C and 2 Pa, respectively.

Using optimal process parameters, the influences of the ratio of Ar/O_2 and the sputtering power on the film deposition rate were analyzed with one-factor analysis. The results show that the partial pressure of oxygen had a great influence on the thin film fabrication. It affected the components of the film and the deposition rate. Consequently, this greatly influenced the characteristics and structure of film.

The increase of the partial pressure of oxygen leads to the decrease of the film deposition rate, and the decrease of the initial slope is small (Fig. 2). It can be noticed that during the sputtering process with the same sputtering pressures, the increase of the partial pressure of oxygen in the atmosphere inevitably leads to the reduction in Ar ion. Then, the bombardment powers of Ar ion and deposition rates decrease. At the same time, the atmospheric oxygen and vanadium ions respond to the target surface and generate the vanadium oxide layer. Moreover, the vanadium oxide yield after sputtering is far less than the metal vanadium, leading to a decline in the deposition rate.

According to Fig. 2, there is an increase in the partial pressure of oxygen followed by the decrease of the deposition rate. When the Ar/O_2 ratio is 100:1, the deposition rate of the VO_x films is the largest, which is 10.23 nm/min. With the increase of oxygen, the pressure of oxygen is gradually maximized, and the deposition rate of the VO_x films reduces. However, before the ratio of Ar/O_2 reaches 100:4, the deposition rate of the VO_x films shows a slow downward trend. When the Ar/O_2 ratio surpasses 100:4, the downward trend of the deposition rate is faster. Therefore, in order to avoid a very low deposition rate of the VO_x films, the ratio of Ar/O_2 must not be greater than 100:4.

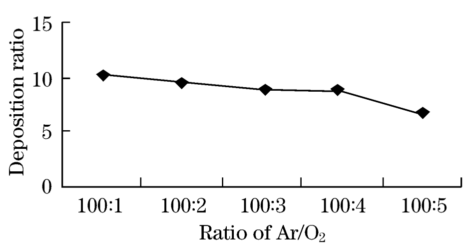

Fig. 2. Relationship between deposition ratio of VO_x and Ar/O_2.

Sputtering power is another important factor of the deposition process. Commonly, more sputtering power results in a higher deposition rate. The number of Ar^+ used to shoot the surface of the vanadium targets increased due to increasing sputtering power, raising the number of collisions between the sputtering gas molecules and atoms in the material. As a result, the film deposition rate increased.

The deposition rate of the VO_x films increases linearly with the increase of sputtering power (Fig. 3). However, the deposition rate of vanadium increased when the vanadium of oxide was less full. A small sputtering power will lead to the decrease in the deposition rate, enhancing the degree of oxidation, and forming a higher amount of vanadium. VO_x film resistance is as much as a megohm resistor. Therefore, 120 W is a more appropriate power.

In the process of film fabrication, it is necessary to anneal. Metal oxide films obtained by sputtering are normally noncrystalline, which means that it contains many defects. However, annealing the thin film can improve the film crystal structure and eliminate the defects. When annealing reduces the crystal boundary, it increases the oxygen vacancy and reduces the film TCR. Therefore, a rapid annealing is also used to apart from the conventional annealing.

Before annealing, the thin film resistance was in the megohm level, which was unstable. The film resistance was more stable after annealing. When the annealing temperature was at around 300 °C, the film resistance was reduced with the increase of the annealing temperature. However, when the annealing temperature was higher than 400 °C, the film resistance increased as the annealing temperature increased. Thin film TCR shows various trends in the different temperature ranges of annealing (Fig. 4).

When the annealing temperature was low, the films had a lower oxidation rate. Then, the deoxidized film rate

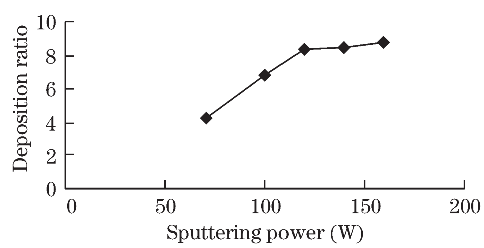

Fig. 3. Relationship of deposition ratio of VO_x and sputtering power.

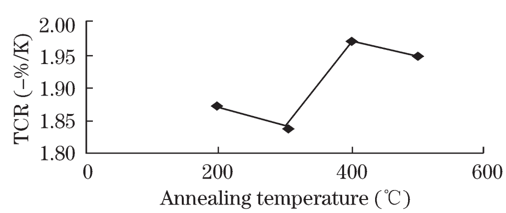

Fig. 4. Relationship between TCR and annealing temperature.

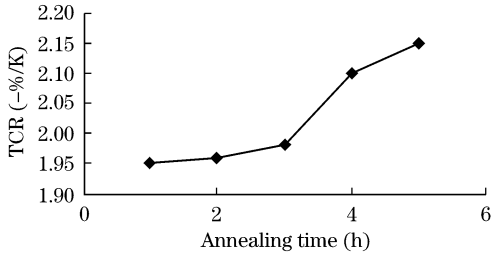

Fig. 5. Relationship between TCR and annealing time.

was higher than the oxidation rate. Therefore, when the films were annealed, deoxidation generated a low-cost VO_x. When the annealing temperature increased more, the film deoxidation became more severe; also, the film resistance reduced. When the annealing temperature was higher than 400 °C, the thin film oxidation rate increased rapidly. It became dominant when the deoxidation rate was outstripped. Thin films annealed at high oxidation will generate vanadium oxide. When the annealing temperature increased, the resistance of the film increased continually. The oxygen that the film oxidation needed mainly came from residual oxygen in the vacuum chamber.

Similar to the annealing temperature, annealing time also has important influences on TCR. The relationship curve between the annealing time and the TCR at the annealing temperature of 400 °C is shown in Fig. 5. Before annealing, the film sheet resistance is 40 kΩ. In the annealing process, the oxygen in the film precipitated, which resulted in the increase in the valence state of vanadium. Experimental results show that the TCR of VO_x annealed for 4 or 5 h is higher, and the main components are VO_2. The increase of the annealing time is conducive to the growth of thinfilm crystallization and formation of a single phase.

In conclude, VO_x films are fabricated by DC magnetron sputtering using a high pure vanadium metal traget (99.99%). The optimized preparation parameters are obtained, the ratio of Ar/O_2 is 100:4, the power is 120 W, the substrate temperature is 300 °C, and the working pressure is 2 Pa. VO_x thin films with a higher TCR are deposited. After vacuum annealing, the TCR values are −2%/K, the maximum is about −3.6%/K. If the TCR needs to be improved, control of the preparation conditions is the most important, which allows the films to contain more VO_2. Annealing can increase the absolute value of TCR. The TCR increases with increasing the annealing temperature. High-temperature annealing could increase the size of the thin film particle, which can eliminate the impact of small particles. However, higher temperature annealing can also cause more defects in the thin films, which is contradictory to the increase of the value of TCR. Therefore, it is necessary to find the best balance between the two aspects.

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