Target voltage behaviour of a vanadium-oxide thin film during reactive magnetron sputtering*

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This paper simulates reactive magnetron-sputtering in constant current mode in a Vanadium-O_2/Ar system equipped with a DC power supply by adopting both kinetics model and Berg's model. The target voltage during the reactive sputtering has been investigated as a function of reactive gas flow. Both experiments and simulations demonstrate a hysteresis curve with respect to the oxygen supply. The time-dependent variation of the target mode is studied by measuring the target voltage for various reactive oxygen gas flows and pre-sputtering times. The pre-sputtering time increases with the increased initial target voltage. Furthermore, a corresponding time-dependent model simulating target voltage changes is also proposed. Based on these simulations, we find some relationships between the discharge voltage behaviour and the properties of the formed oxide. In this way, a better understanding of the target voltage changes during reactive sputtering can be achieved. We conclude that the presented theoretical models for parameter-dependent case and time-dependent case are in qualitative agreement with the experimental results and can be used to comprehend the target voltage behaviour in the deposition of vanadium oxide thin films.

Keywords: Berg's model, time dependence, target voltage, vanadium oxide
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1. Introduction

As one of the fascinating materials with excellent physical and chemical properties, vanadium oxide (VO) thin films have been studied extensively.[1,2] Reactive-sputtering is a common process for deposition of oxides, carbides and nitrides.[3] The VO films have been widely prepared by the reactive DC magnetron-sputtering method. The partial pressure of the sputtering gas, the sputtering time, the substrate temperature and the sputtering voltage are main process parameters determining the film properties when VO thin films are deposited by reactive DC magnetron-sputtering. Among these parameters, the discharge voltage perhaps is the most accessible parameter.

Many theoretical researches have been taken to understand and to improve the reactive-sputtering deposition. Most of the theoretical models are of steady state. Steady-state hysteresis is reasonably well described by Berg's model.[3,4] More recently, extensions to this model have been published[5−11] including models which consider the target voltage as a function of reactive gas flow. Some models have considered the information of operation process. Kusano *et al.* proposed a time-dependent simulation model[12,13] and theoretically illustrated hysteresis curves of the oxygen partial pressure versus the oxygen flow rate. Zhu *et al.*[14] used the kinetics model to simulate the reactive-sputtering deposition under voltage control.

Our investigation of time-dependent changes in the target voltage and in the compound fraction on the target are more comprehensive, which includes both pre-sputtering and reactive-sputtering processes. The influence of the processing parameters on the target voltage behaviour is discussed. Meanwhile, theoretical and experimental result are also compared.

2. Theoretical basis

2.1. Berg's model

The mathematical model describing the sputtering system is shown in Fig. 1.[1] The total supply rate of the reactive gas (oxygen) is denoted as Q. To be able to simulate the system more efficiently, Wei *et al.*[1] have made some assumptions in the model. First the sputtered material is assumed to be distributed

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uniformly on the target surface, which is divided into two parts (see Fig. 1). Here θ_t denotes the fraction of the target surface consisted of VO, the fraction $(1-\theta_t)$ of the target surface containing unreacted metal vanadium. Second the substrate can be divided into two parts. The θ_c fraction is assumed to be covered by VO.

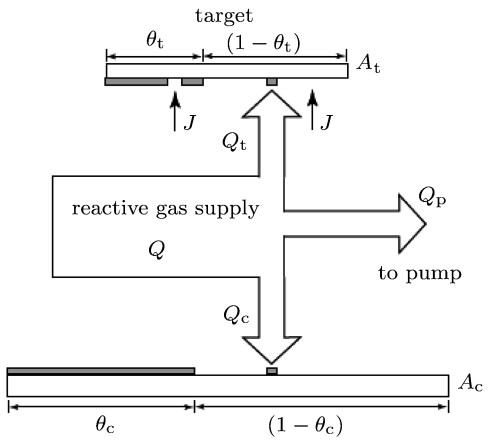


Fig. 1. Schematic diagram of a simple reactive-sputtering system.

The partial pressure of reactive gas in the chamber is uniform, denoted as P. The reactive-sputtering is described as follows: From gas kinetics, the relationship between F (the amount of gas molecules per unit area) and P is

$$F = \frac{P}{\sqrt{2kT\pi m}}, \tag{1}$$

where k is the Boltzmann constant, T is the temperature and m is the mass of the gas molecule. It is assumed that no reaction between underlying target elemental atoms and the reactive gas takes place at the compound fraction θ_t of the target area. A steady-state equation for the target may be defined as

$$\frac{J}{q}Y_c\theta_t = \alpha 2F(1-\theta_t), \tag{2}$$

where Y_c is the sputtering yield of compound molecules from the compound-covered fraction θ_t of the target, α is the sticking coefficient, q is the elementary electronic charge, and J is the Ar^+ current density. From these expressions we can obtain

$$\theta_t = \frac{2\frac{P}{\sqrt{2kT\pi m}}\alpha}{2\frac{P}{\sqrt{2kT\pi m}}\alpha + \frac{J}{q}Y_c}. \tag{3}$$

Based on the fact that target voltage U depends on both the secondary emission coefficient γ and the target poisoning, Pflug *et al.*[15] suggested the expression

$$\gamma = [\gamma_m(1-\theta_t) + \gamma_c\theta_t]\frac{U}{U_0}, \tag{4}$$

where γ_m and γ_c are the secondary electron emission coefficients for the metal and the compound areas of the target surface. The U_0 is a reference voltage required for keeping the equation dimensionless. Thus, by this equation, U is calculated as a function of θ_t.

2.2. Time-dependent model

2.2.1. Sputtering in the atmosphere of Ar–O_2

According to the kinetics model for reactive sputtering, the time dependence of the compound coverage on the target is given by

$$\frac{d\theta}{dt} = \frac{1}{N_0}(V_f - V_g), \tag{5}$$

where N_0 is the areal density of atoms on the target surface, V_g is the sputtering rate of compound from the target, V_f is the forming rate of compound onto the target, at time t.

$$\theta(t+\Delta t) = \theta(t) + \frac{d\theta_t}{dt}.\Delta t. \tag{6}$$

The sputtering rate of compound from the target V_g and the forming rate of compound onto the target V_f are usually expressed as

$$V_g = JY_c\theta_t, \tag{7}$$

$$V_f = \beta\alpha F(1-\theta_t), \tag{8}$$

where Y_c is the sputtering yield of compound, α is the the probability (sticking coefficient) for the oxygen molecule to react with vanadium atom at the $(1-\theta_t)$ fraction of the target, β is the number of VO molecules that one reactive gas molecule can form.

The consumption of the reactive gas at the target Q_t can be expressed as

$$Q_t = \alpha F(1-\theta_t)A_t. \tag{9}$$

The remaining part of the reactive gas Q_p will escape from the processing chamber through the pumping system. Assuming a pumping speed of S, we obtain

$$Q_p = PS. \tag{10}$$

In the kinetics model, the partial pressure of the reactive gas P is not only determined by the reactive gas flow rate fed into the chamber and the flow rate

pumped out of the chamber, but also determined by the gettering effect

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{Q - Q_\mathrm{t} - Q_\mathrm{p}}{V_\mathrm{c}}. \tag{11}$$

Here, P and Q is the partial pressure and the flow rate of the reactive gas, respectively, and V_c is the volume of chamber.

2.2.2. Pre-sputtering (sputtering in pure Ar atmosphere)

In the experiment, the vanadium target is pre-sputtered in pure Ar gas to clean the target surface. In this case, the forming rate of compound onto the target V_f is equal to zero. And Eq. (5) is rewritten as

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = \frac{-V_\mathrm{g}}{N_0}. \tag{12}$$

Meanwhile, the flow rate of the reactive gas Q also reaches zero. Equation (11) can be rewritten as

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{-Q_\mathrm{t} - Q_\mathrm{p}}{V_\mathrm{c}}. \tag{13}$$

From the Eqs. (12) and (13) above, we can show that $\mathrm{d}\theta/\mathrm{d}t < 0$, $\mathrm{d}P/\mathrm{d}t < 0$. Therefore, it can be derived that the fraction of compound and partial pressure will decrease with the increase of time t.

3. Experiment

3.1. Steady states: oxygen gas flow dependent relationship

The VO thin films were deposited by reactive DC magnetron-sputtering in a planar magnetron-sputtering system as shown in Fig. 2. Each magnetron acted as a cathode, and a grounding bias voltage was applied to the substrate. The magnetron sources, running at a power of 120–150 W, were placed at a distance of 55 mm away from the substrate and tilted 30 degrees away from the substrate normal. To avoid cross contamination of the three targets, baffle plates were mounted on the other two magnetrons. A resistive heater was mounted above the substrate so that the temperature, measured by a chromel–alumel thermocouple, could be varied from room temperature up to 700 °C. The target was 99.98% pure vanadium. The reactive sputtering gas was a mixture of Ar (99.999%) and O_2 (99.9999%). The deposition temperature is 300 °C. The effective pumping speed was of 10 l/s and the argon flow was 6 sccm (sccm denotes cubic centimeter per minute at standard temperature and pressure).

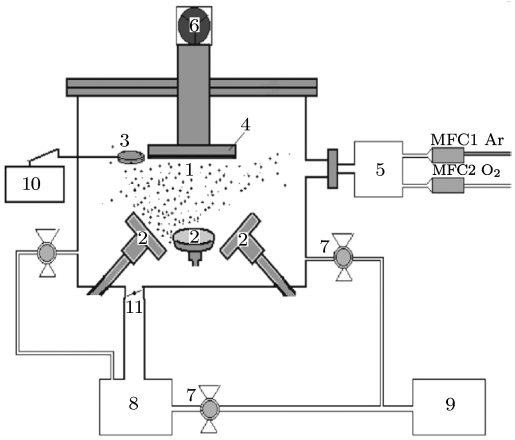


Fig. 2. Schematic illustration of experimental set-up: (1) substrate; (2) magnetron sources; (3) quartz microbalance; (4) resistive heater; (5) gas supply; (6) rotating controller; (7) small angle valves; (8) turbo pump; (9) rotary pump; (10) frequency meter; (11) slide valve.

3.2. Kinetics: time-dependent relationship

The vanadium target was pre-sputtered in pure Ar gas to clean the target surface. Next, the flow of oxygen was changed according to the DC power to the target.

The D08-2B/ZM gas mass flux controllers (MFC1, MFC2) were used to control the flux of oxygen and the flux of argon introduced into the chamber. The target voltage was measured and shown by a FLUKE 8842 multimeter.

4. Results and discussion

The values of all parameters in this model are as follows: target area $A_\mathrm{t} = 0.02$ m^2, substrate area $A_\mathrm{s} = 0.05$ m^2, sticking coefficient $\alpha = 1$, sputtering yield of metal from metallic surface $Y_\mathrm{m} = 0.41$, sputtering yield of metal V from the compound VO $Y_\mathrm{c} = 0.04$, discharge current $I = 0.5$ A, pumping speed $S = 40$ L/s and $T = 573$ K.

4.1. Oxygen flow dependent relationship

Figures 3(a) and 3(b) show the target voltage versus oxygen flow from simulations and experiments, respectively. An increase in the supply of oxygen will gradually leads to an increase in the partial pressure

of the reactive gas. As the partial pressure increases, θ_t will enlarge, causing the increment of target. The hysteresis in both experiment and simulation appears at this stage of increasing and decreasing the reactive gas flow. In particular, at low oxygen flow, almost all the available oxygen is gettered by the sputtered metal. As a result, no essential change from the background level in reactive gas pressure and in target voltage is observed. This situation persists until the flow reaches a critical value, where the flow rate of the oxygen into chamber becomes higher than the gettering rate of the sputtered metal, which then introduces a sudden increase in the partial pressure of the oxygen.

Target voltage changes when the target becomes fully poisoned due to the increase or the decrease of the secondary electron emission coefficient of the oxided target surface.[16] It should be noticed that in Eq. (4), γ_m may be either smaller or larger than γ_c. Consequently, the voltage may either increase or decrease with a larger supply of reactive gas. In the case of vanadium, the target voltage becomes higher with higher reactive gas partial pressure. As it can be seen in Fig. 3(a), there is a sharp increase in the target voltage when the target becomes poisoned. A closed hysteresis loop is formed in this way.

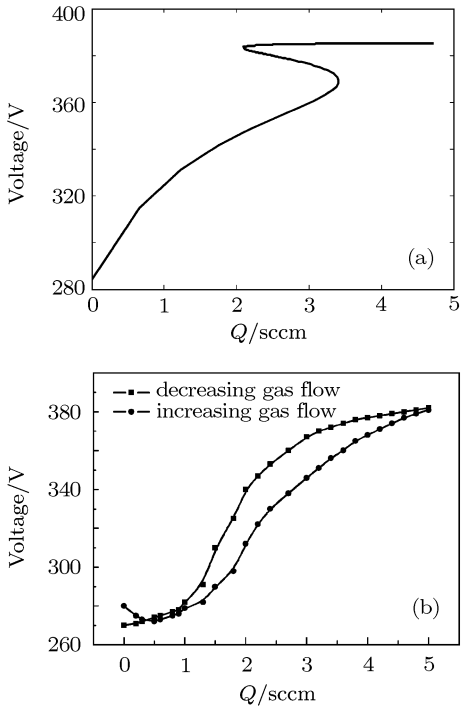


Fig. 3. (a) Calculated target voltage behaviour versus the reactive gas flow. (b) Experimental results of target voltage behaviour versus the reactive gas flow.

The experimental dependences of the discharge voltage on oxygen flow are depicted in Fig. 3(b). This figure clearly illustrates the difference between increasing and decreasing the supply of oxygen. However, it does not exhibit the S-shaped form, but rather show a hysteresis effect. Actually, there is a short decrease of target voltage when the oxygen flow increases at the beginning of this process. The reason may be as follows. Our model bases on the assumption that the initial θ_t on the target reaches zero after pre-sputtering process. Nevertheless, there are some compound remained on the target which cause a decrease of θ_t temporarily in the beginning of the experiment. Therefore, target voltage also decreases with the change of θ_t in this region.

4.2. Time dependent relationship

The target voltage behaviour during pre-sputtering in pure Ar gas at different values of oxygen gas flow is shown in Fig. 4. During the reactive sputtering of VO films, vanadium target was first pre-sputtered in pure Ar gas to clean the target surface. We refer the initial voltage as V_{O-Ar}. Then, we refer target voltage in Ar–O_2 plasma as V_{Ar}. The value of V_{O-Ar} and the time for pre-sputtering is determined by experiment. Under this condition, the oxide coverage on the target will gradually decrease in the pre-sputtering process. As θ_t decreases, V_{O-Ar} reduces.

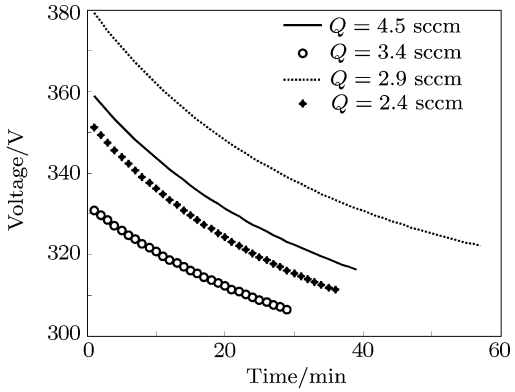


Fig. 4. Calculated initial voltage and target voltage versus time at pre-sputtering process.

The oxide coverage of the target as a function of time in reactive-sputtering process is shown in Fig. 5. It is assumed that initial coverage almost reaches zero. The coverage increases sharply for the first 5 min, and then gradually increases for the next 10–15 min. In the region of time > 20 min, the increment of coverage decreases in comparison with that for time < 15 min. The phenomena occurred at the target surface for the first 10 min seem to be most crucial in the process. As oxygen flow Q increases, more amount of oxygen is consumed by target surface oxidation, which results in an increase in the fraction of compound on the target.

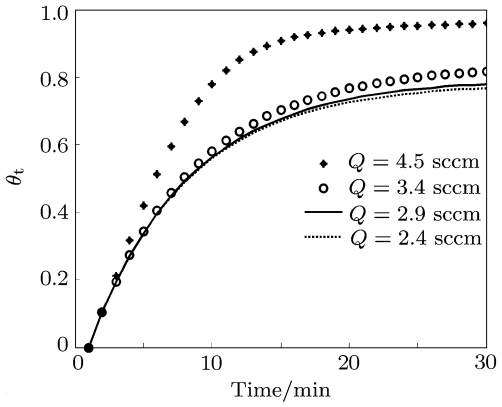


Fig. 5. Calculated fraction of compound on the target versus time and oxygen gas flow at reactive sputtering process.

Changes of target voltage during sputtering for various oxygen flows are shown in Fig. 6. We refer the initial voltage as V_{O-O_2}. The value of this parameter is approximately 315 V according to the experimental data. Then, we refer target voltage in Ar–O_2 plasma as V_{O_2}. The of the voltage starts ($t = 0$ min) with the start of the oxygen flow. In particular, the increase in the target voltage corresponds well with the increase in oxide coverage on the target. Drastic changes occur in the first 10 min. For the time region > 10 min, the condition becomes stable. In this region, no remarkable change occurs on the target and target voltage reaches a stable value.

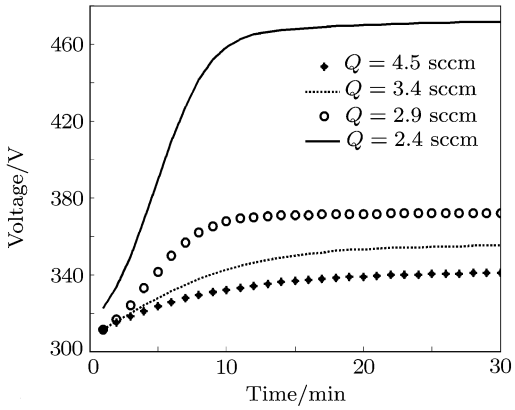


Fig. 6. Calculated target voltage versus time and oxygen gas flow at reactive sputtering process.

In this constant current system, the cathode voltage is proportional to time t. Moreover, with the increase of oxygen gas flow, V_{O_2} is obviously increased. Especially under the condition of $Q = 4.5$ sccm, V_{O_2} approximates to be 480 V.

The results of the simulations in comparison with experimental findings are shown in Fig. 7. It is clearly shown that the behaviours exhibite discontinuities which include the pre-sputtering (Fig. 4) and the sputtering with Ar–O_2 atmosphere (Fig. 6). According to the simulation using a variety of initial values of the target voltage V_{O-Ar} as shown in Fig. 7(b), the duration of pre-sputtering is strongly dependent upon the initial target voltage V_{O-Ar}. In other words, different initial target voltages need different pre-sputtering time.

The model qualitatively explains the sputtering process. The experimental data for sputtering are in reasonably good agreement with that of the simulations. However, there is a difference between the experimental and the simulated voltage when $Q = 4.5$ sccm in the time range of 25–40 min. In the first 25 minutes, the compound-covered fraction slightly decreases, this fact differs from simulations results. This deviation is considered to be caused by the target surface being oxidized to mix-valence oxides in the experiment.

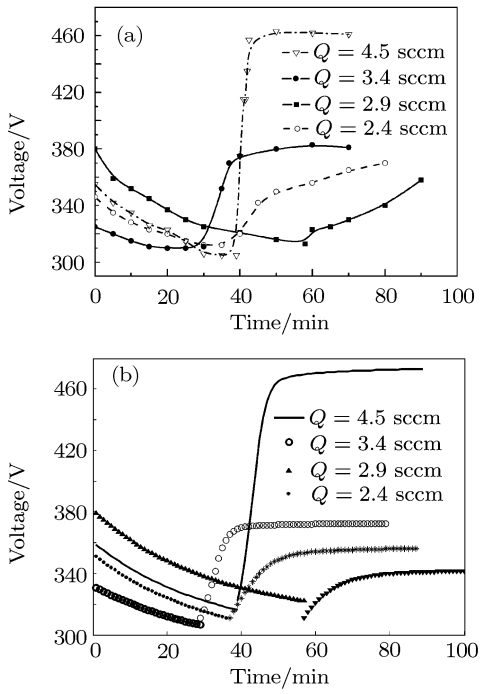


Fig. 7. (a) Time dependence of target voltage behaviour during pre-sputtering and reactive sputtering process. (b) calculated time dependenc of target voltage behaviour during pre-sputtering and reactive sputtering process.

5. Conclusion

Control of the reactive sputtering process can be carried out by controlling either the flow of the reactive gas or the duration of the sputtering, which are called parameter-dependent and time-dependent behaviours. In the flow control mode, both experiments

and simulations show a pronounced hysteresis effect on the target voltage during reactive sputtering of VO thin film. The simulated results accord well with the experimental results obtained in this work. The time-dependent variation of the target of a VO system is investigated by measuring the target voltage for various reactive oxygen gas flows and pre-sputtering times. The experimental findings are compared with results from computer simulations of the corresponding process. The theoretical calculations are based on time-dependent model involved both pre-sputtering behaviours and reactive sputtering ones, which have been proven to be able to correctly describe the target behaviour and to predict most of the experimental results. These investigations are shown to be useful for understanding the target voltage behaviour of reactive sputtering VO thin films.

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