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Simulation of Reactive Sputter Deposition of TiO_2 Films

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The reactive sputter deposition of titanium dioxide films in $Ar + O_2$ atmosphere is considered. The processes of sputtering, adsorption and heterogeneous reactions are included in the model. The partial pressure of O_2 molecules is calculated as a function of the flow rate of the reactive gas, pumping speed, sputtering yields of Ti atoms and TiO_2 molecules, and reaction rate constant. The dependences of concentrations of TiO_2 molecules on the target and substrate surfaces and deposition rate upon the O_2 flow rate are obtained. Special attention is given to the phenomenon of formation of a hysteresis loop. It is found that the increase of the pumping speed, chamber volume, reaction rate constant, and sputtering yield of TiO_2 molecules as well as decrease of the target surface area and sputtering yield of Ti atoms reduce the size of the hysteresis loop.

Keywords: reactive sputter deposition; TiO_2; hysteresis.

INTRODUCTION

Titanium dioxide is used in heterogeneous catalysis, as a photocatalyst, in solar cells for the production of hydrogen and electric energy, as gas sensor, as a corrosion-protective coating, as an optical coating, and in electric devices such as varistors. It plays a role in the biocompatibility of bone implants and finds applications in Li-based batteries and electrochromic devices [1]. The properties of the TiO_2 film prepared by reactive sputter deposition depend not only on the preparation technique but also on the sputtering conditions, such as discharge pressure, partial pressure of the reactive gas, and discharge current. Many experimental and theoretical investigations have improved the understanding of reactive sputter deposition system [2 – 8]. When compounds are reactively sputtered from metal targets using combinations of an inert gas, typically argon, and a reactive gas, there is a hysteresis relationship between the deposition rate of material and the reactive gas flow. Starting from low flow rates of the reactive gas and proceeding to higher flow rates, the deposited material will transition abruptly from a metallic mode to an oxide mode. Conversely, starting from high flow rates of the reactive gas and proceeding to lower flow rates, the deposited material will transition abruptly from an oxide mode to a metallic mode [9]. Due to a hysteresis in the dependence of the deposition rate upon the flow rate of the reactive gas, instabilities in the sputter process may occur. In most practical applications, the reactive sputter deposition process has to be controlled by an external regulating circuit such as plasma emission monitoring [10]. Numerical simulations of reactive sputter deposition system are used to optimize deposition processes.

In this work, the dependence of the partial pressure of O_2 molecules upon the flow rate of the reactive gas is calculated by extrapolation from experimental data. The dependences of concentrations of TiO_2 molecules on the target and substrate surfaces and deposition rate upon the O_2 flow rate are obtained. The parameters that influence the size and position of the hysteresis loop are determined.

MODEL

The reactive sputter deposition of TiO_2 in the $Ar + O_2$ atmosphere is considered. The proposed model is based on the independent analysis of processes taking place on the target and substrate surfaces. O_2 molecules present in the gas phase react with Ti atoms on the target and substrate surfaces and the following reaction takes place:

$$Ti + O_2 \rightarrow TiO_2 . \qquad (1)$$

This reaction is characterized by the reaction rate constant k_1. Reaction defined by Eq. (1) is a resultant reaction, which includes the adsorption of O_2 molecules on the surface, dissociation of adsorbed O_2 molecules, and reaction of O atoms with Ti atoms on the surface. Ti atoms and TiO_2 molecules are sputtered from the target surface during ion bombardment. These processes are characterized by frequency probabilities of sputtering:

$$\omega_i = Y_i I_0 / C , \qquad (2)$$

where Y_i is the sputtering yield of the i-th component, I_0 is the ion flux, and C is the concentration of surface atoms ($C = 1.48 \times 10^{19}$ m^{-2}). Let us assume that all sputtered Ti atoms and TiO_2 molecules are deposited on the substrate surface.

Two components exist on the target surface: Ti and TiO_2 with relative concentrations $c_1 = [Ti]/C$ and $c_2 = [TiO_2]/C$, respectively; two components exist on the substrate surface: Ti and TiO_2 with relative concentrations $c_3 = [Ti]/C$ and $c_4 = [TiO_2]/C$, respectively. The relative concentrations of components on the target and substrate surfaces must fulfill the following conditions: $c_1 + c_2 = 1$ and $c_3 + c_4 = 1$. The following system of equations includes rate expressions of processes mentioned earlier and describes the kinetics of concentrations of components in the gas phase and on the target and substrate surfaces:

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$$\begin{cases} \frac{dn}{dt} = \frac{\Phi}{V} - \frac{k_1 n C\left(S_T c_1 + S c_3\right)}{V} - En, \\ \frac{dc_1}{dt} = -k_1 n c_1 + \omega_2 c_2, \\ \frac{dc_3}{dt} = -\left(k_1 n + \frac{S_T \omega_2 c_2}{S}\right) c_3 + \frac{S_T \omega_1 c_1 c_4}{S}, \end{cases} \qquad (3)$$

where n is the concentration of O_2 molecules, S is the substrate surface area, S_T is the target surface area, Φ is the O_2 flow rate measured in molecules (s^{-1}), V is the chamber volume, and E is the frequency probability of exhaust. The partial pressure of O_2 molecules is calculated using expression $p = nkT$, where k is the Boltzmann constant and T is the temperature ($T = 300$ K). The initial conditions are following: $c_1 = 1$, $c_2 = 0$, $c_3 = 1$, $c_4 = 0$ for increasing flow rate; and $c_1 = 0$, $c_2 = 1$, $c_3 = 0$, $c_4 = 1$ for decreasing flow rate.

Let us consider processes on the target surface only ($S = 0$). When the condition $k_1 n >> \omega_2$ is assumed, the following expression of concentration of O_2 molecules in the gas phase at steady-state regime is obtained:

$$n = \left(\Phi - S_T C \omega_2\right) / EV. \qquad (4)$$

The concentration of O_2 molecules linearly increases with the increase of the O_2 flow rate. The critical O_2 flow rate value at which the concentration starts to increase depends on the target surface area, concentration of surface atoms, and frequency probability of sputtering of TiO_2 molecules. The critical O_2 flow rate value for the substrate surface depends on the frequency probability of sputtering rate of Ti atoms. Let us assume that substrate surface consumes the O_2 molecules exclusively from the gas phase. When the substrate surface becomes oxidized, the target surface consumes a residue of O_2. The deposition rate is proportional to the sum of sputtering rates of Ti atoms and TiO_2 molecules from the target surface:

$$V = h_0 S_T \left(\omega_1 c_1 + \omega_2 c_2\right) / S, \qquad (5)$$

where $h_0 = 2.60$ Å is the thickness of a monolayer.

RESULTS AND DISCUSSION

The experimentally measured dependence of the O_2 partial pressure upon the O_2 flow rate [11] is used for the calculation of deposition rates. The experimental conditions were following: the power supplied to the target 600 W, the partial pressure of Ar gas 0.9 Pa, the target surface area 0.031 m^2, the substrate surface area 0.20 m^2, and the pumping speed 0.050 $m^3 s^{-1}$. Experimental [11] and theoretical dependences of the O_2 partial pressure upon the O_2 flow rate are shown in Fig. 1. The following values of constants and frequency probabilities are used: $k_1 = 1.0 \times 10^{-16}$ $m^3 s^{-1}$, $\omega_1 = 1.56$ s^{-1}, $\omega_2 = 0.068$ s^{-1}, $S = 0.20$ m^2, $S_T = 0.031$ m^2, $E = 0.34$ s^{-1}, $V = 0.20$ m^3. The target and substrate surface areas and the frequency probability of sputtering of TiO_2 molecules are obtained from experimental results [11]. The dependences of concentrations of TiO_2 molecules on the target and substrate surfaces upon the O_2 flow rate are shown in Fig. 2. It is observed that the concentration of TiO_2 molecules on the target surface unevenly changes at a critical value of the O_2 flow rate. The dependence of the deposition rate upon the O_2 flow rate is shown in Fig. 3. The obtained results are in an agreement with the experimental measurements [11].

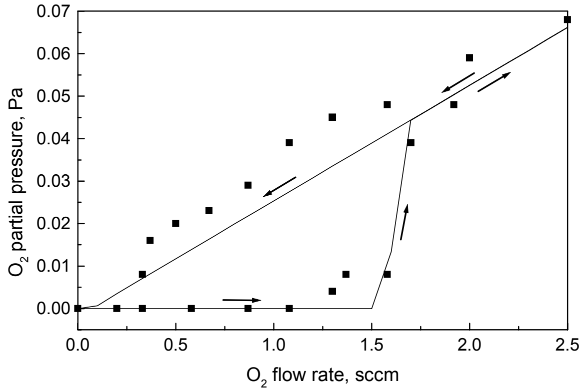

Fig. 1. Experimental [11] (points) and theoretical (curve) dependences of the O_2 partial pressure upon the O_2 flow rate

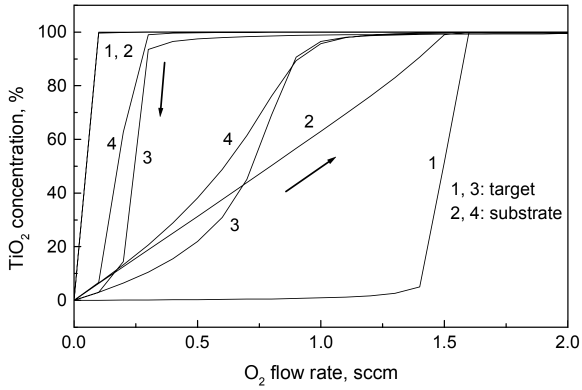

Fig. 2. The dependences of the concentrations of TiO_2 molecules on the target and substrate surfaces upon the O_2 flow rate at different values of the frequency probability of exhaust E: 1, 2 – 0.34 s^{-1}, 3, 4 – 34 s^{-1}

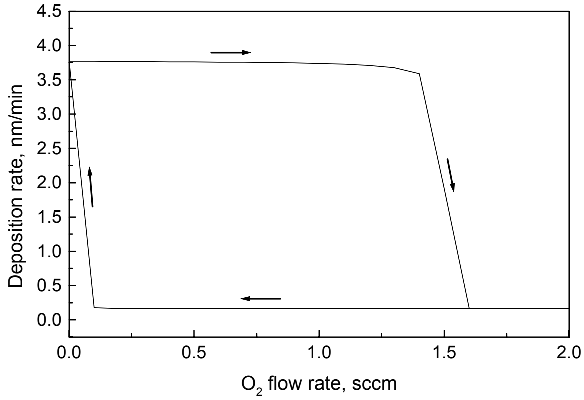

Fig. 3. The dependence of the deposition rate upon the O_2 flow rate

Experimentally [12], it was found that the size of the hysteresis loop decreases with the increase of the pumping speed. The uncertainties in the flux of Ti atoms to the surface [11] and in the partial pressure of O_2 molecules [13] decrease with the increase of the pumping speed. In order to determine parameters that influence the decrease of the size of the hysteresis loop, the dependences of concentrations of TiO_2 molecules on the target and substrate surfaces upon the O_2 flow rate at a 100 times higher frequency probability of exhaust (or chamber volume) are calculated (Fig. 2). The observed difference between concentrations of TiO_2 molecules on the target and substrate surfaces is less. When the target surface area or sputtering yield of Ti atoms decrease, less atoms are sputtered, and subsequently less O_2 molecules are required to cover the surfaces with oxide molecules. As a result, the size of the hysteresis loop decreases (Fig. 4).

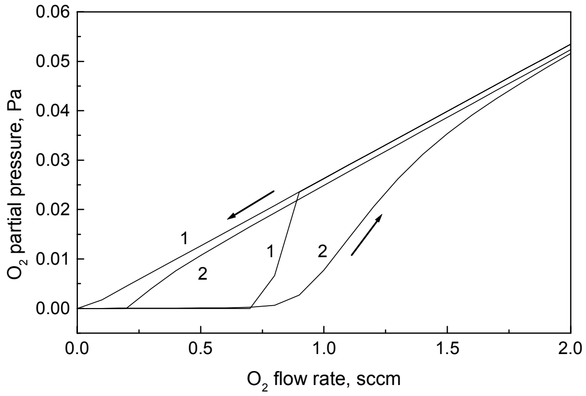

Fig. 4. The dependences of the O_2 partial pressure upon the O_2 flow rate: 1 – at a two times lower target surface area S_T; 2 – at a 100 times lower reaction rate constant k_1

The analogous results are obtained when the reaction rate constant k_1 decreases. The increase of the sputtering yield of TiO_2 molecules from the target surface hastens a transition from the oxide to metallic mode, and decreases the size of the hysteresis loop. The obtained results are in an agreement with the experimental measurements [12, 14] and can be used to avoid the hysteresis effect.

CONCLUSIONS

1. The position of the hysteresis loop depends on the sputtering yields of Ti atoms and TiO_2 molecules, and target surface area.
2. The increase of the pumping speed, chamber volume, and sputtering yield of TiO_2 molecules as well as the decrease of reaction rate constant, target surface area, and sputtering yield of Ti atoms decrease the size of the hysteresis loop.

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