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Influence of a Revolutionary Substrate on Hysteresis Effect in Reactive Sputtering Deposition of Vanadium Oxide

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Reactive sputter processes frequently exhibit stability problems. The cause of this is that these processes normally exhibit hysteresis effects in the processing curves. Eliminating or decreasing the hysteresis would significantly simplify the use of reactive sputtering processes. In this work, we present reactive sputtering deposition modeling of vanadium oxide with a revolutionary substrate, aiming to study the influence of it on hysteresis effect. Based on this modeling, the fractions of V, V_2O_3, VO_2, V_2O_5 at the target surface and target voltage have been investigated as a function of reactive gas flow during the reactive sputtering. The substrate area was replaced by a new parameter of effective area of substrate A_s which was calculated as a sum of contributions from the substrate area at each cell of time. From the modeling results, it is suggested that the effective area of the substrate was reduced for reactive sputtering with revolutionary substrate, thus the hysteresis width would be decreased. This has been experimentally verified by reactive sputtering deposition of VO_x. Besides, the fundamental explanation to this behavior as well as the experimental verification is presented.

Keywords: reactive sputtering, modeling, hysteresis effect, revolutionary substrate.

1. INTRODUCTION

Reactive-sputtering is a commonly used process for deposition of oxides, carbides and nitrides [1 – 3]. It is a well known fact that the relationship between the reactive gas flow and the other processing parameter is very complex, non-linear and usually exhibits hysteresis effect. The steady-state hysteresis has been extensively studied and existing models are capable to describe and predict most processing behavior [4 – 7]. So far, much work has been done to decrease the hysteresis by increasing the pumping speed to quite high value [5], introducing an additional reactive gas supply in the process [8 – 9], or reducing the size of the target sputter erosion zone [10]. In this article, a new way to design a system where this hysteresis is decreased has been identified. On the other hand, in order to ensure uniform thickness film, some manufacturers have introduced moving substrate with rotation and revolution in the magnetron sputtering system [11]. However, no attention has been paid on the performance of the planetary substrate in reactive sputtering process, especially the effect on hysteresis width. According to the results of theoretical modeling, a revolutionary substrate has significant effect on the hysteresis effect. We present the cause of the hysteresis reduction as well as experimental verification of the phenomena.

2. MODEL

2.1. Fundamental modeling of reactive sputtering

The numerical model used in this paper is described in detail in [12]. In summary, the model, based on Berg's model, is represented by a set of balance equations that describe the reactions of destruction and formation of compounds on the target surface and collecting area. Solving this set of nonlinear equations gives the chemical area in either stationary or nonstationary conditions. During simulations, the film structure is assumed to be composed of a mixture of V, V_2O_3, VO_2, and V_2O_5. The target surface can be divided into four parts. θ_{t1}, θ_{t2}, θ_{t3} and θ_{t4} denote fraction of V, V_2O_3, VO_2 and V_2O_5 on the target respectively.

According to the modelling we presented in [12], the consumption (number of oxygen molecules per unit time) at the target Q_t can be obtained from Eq. 1.

$$\begin{aligned}
&Q_{t1} = 2\alpha_1 F A_t \theta_{t1} / l_2 ;\\
&Q_{t2} = 2\alpha_2 F A_t \theta_{t2} /(l_3 - l_2) ;\\
&Q_{t3} = 2\alpha_3 F A_t \theta_{t3} /(l_4 - l_3) ;\\
&Q_t = Q_{t1} + Q_{t2} + Q_{t3} ,
\end{aligned} \tag{1}$$

where A_t is the target area; F represents neutral reactive molecules/ (unit area and time); α_1-α_3 are the probability (sticking coefficient) for the oxygen molecule to react with V, V_2O_3, and VO_2 respectively. l_2-l_4 are the stoichiometry of V_2O_3, VO_2 and V_2O_5, respectively. Q_{t1}- Q_{t3} are reactive gas molecules consumed by V, V_2O_3, and VO_2 on the target, respectively.

While the consumption Q_s at the collecting area A_s can be expressed by Eq. 2:

$$\begin{aligned}
&Q_{s1} = 2\alpha_1 F A_s \theta_{s1} / l_2 ;\\
&Q_{s2} = 2\alpha_2 F A_s \theta_{s2} /(l_3 - l_2) ;\\
&Q_{s3} = 2\alpha_3 F A_s \theta_{s3} /(l_4 - l_3) ;\\
&Q_s = Q_{s1} + Q_{s2} + Q_{s3} ,
\end{aligned} \tag{2}$$

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where Q_{s1}- Q_{s3} are reactive gas molecules consumed by V; V_2O_3, and VO_2 on the substrate, respectively.

The remaining part Q_p of the reactive gas will escape from the processing chamber through the pumping system.

$$Q_p = \frac{P N_a}{R_r T} S, \tag{3}$$

where P is the partial pressure of oxygen; N_a is Avogadro constant; R_r is general gas constant; T is the temperature; S is the pumping speed.

The total supply rate of the reactive gas is denoted Q_{tot}.

$$Q_{tot} = Q_t + Q_s + Q_p. \tag{4}$$

From the above equations, it is seen that the coverage fraction (θ_{t1}, θ_{t2}, θ_{t3} and θ_{t4}) is related to both substrate effective area (A_s) and reactive gas flow (Q_{tot}).

2.2. Effective area of substrate

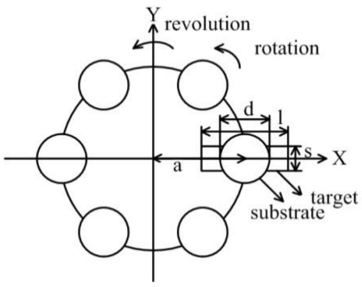


Fig. 1. Schematic of magnetron sputtering system with a revolutionary substrate

In order to determine parameter that influences the size of the hysteresis loop, the effective area of substrate was calculated.

Fig. 1 shows the schematic of magnetron sputtering system with a revolutionary substrate.

P is a random point on the substrate. Note that the equation of the pathway of the point P (R, p) on the substrate can be expressed by

$$x = R\cos(p) + a\cos(\omega_{rev}t); \tag{5}$$

$$y = R\sin(p) + a\sin(\omega_{rev}t), \tag{6}$$

where ω_{rev} is revolution angular velocity, t time, R is the distance from arbitrary point P to the center of the substrate, p is the polar angle of point P. The target is a square. As is shown in Fig. 1, l is the length of the target while s is the width of target, the distance from the center of revolution to that of the target is a, the diameter of the substrate is d. Meanwhile, the abscissa is cross the center of target and revolution. l and s are 244 mm and 54 mm respectively. d is 150 mm, a is 175 mm. Once the relationship of the position of point P and time t is obtained, it is possible to calculate the average or effective area for the substrate A_s.

For simplicity, we assume that the substrate effective area is the part between the top and bottom lines of target (been marked by shadow region in Fig. 2 b and Fig. 2 c). In order to calculate A_s, time t is divided into cells. For each cell of time, the point P is at different positions. Therefore, the sum effective area of substrate can be calculated as a sum of contributions from the substrate area at each cell of time. In this case, three relationships (as shown in Fig. 2) between the substrate and the target should be discussed:

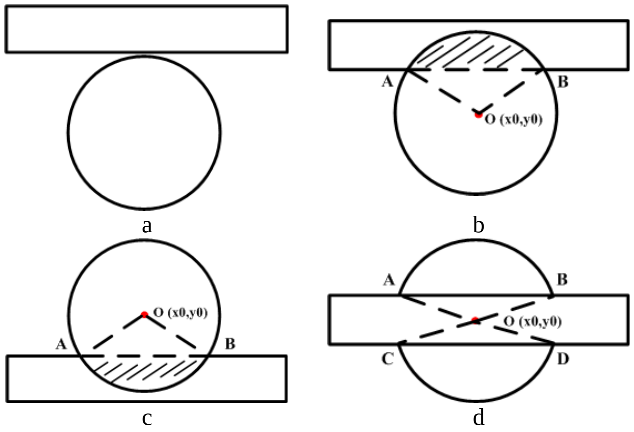


Fig. 2. The different relationship between target and substrate: a – no interaction; b, c – two interaction points; d – four interaction points

If the substrate and target have no interaction, as shown in Fig. 2 a, A_s is equal to zero.

In Fig. 2 b, c the substrate effective area is equal to the area of Fan AOB take away ΔOAB. Therefore, the equation of A_s is

$$A_s = \pi R^2 (\frac{\theta_{AOB}}{2\pi}) - \frac{\frac{1}{2} L_{AB} L_{AB}}{\tan(\theta_{AOB}/2)}. \tag{7}$$

Under this condition, two situations should be considered:

A. As shown in Fig. 3 a, A_s can be expressed by $S = S_{substrate} - \hat{S}_{AB} - \hat{S}_{CD}$. This leads to the following equation:

$$A_s = \pi R^2 - [\pi R^2 (\frac{\theta_{AOB}}{2\pi}) - \frac{\frac{1}{2} L_{AB} L_{AB}}{\tan(\theta_{AOB}/2)}] - [\pi R^2 (\frac{\theta_{COD}}{2\pi}) - \frac{\frac{1}{2} L_{CD} L_{CD}}{\tan(\theta_{COD}/2)}]. \tag{8}$$

B. As shown in Fig. 3 b, A_s can be expressed by $S = \hat{S}_{ACDB} - \hat{S}_{CD}$. A_s can be expressed by the following equation:

$$A_s = [\pi R^2 (\frac{\theta_{AOB}}{2\pi}) - \frac{\frac{1}{2} L_{AB} L_{AB}}{\tan(\theta_{AOB}/2)}] - [\pi R^2 (\frac{\theta_{COD}}{2\pi}) - \frac{\frac{1}{2} L_{CD} L_{CD}}{\tan(\theta_{COD}/2)}]. \tag{9}$$

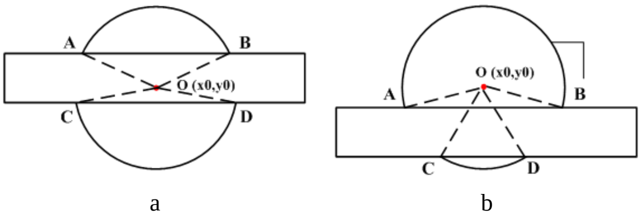


Fig. 3. Four interaction points between target and substrate. a – O is inside of the target; b – O is outside of the target

Then, the average value of the substrate area can be expressed by the following equation:

$$A_{s\,eff} = \frac{\sum_{t=0}^{t} A_s}{t}. \tag{10}$$

3. EXPERIMENTAL

VO_x thin films were deposited by reactive DC magnetron sputtering in a planar magnetron-sputtering system with a revolutionary substrate, as shown in Fig. 1. Each magnetron acted as a cathode, and a grounding bias voltage was applied to the substrate. The target was 99.98 % pure vanadium. The reactive sputtering gas was a mixture of Ar (99.999 %) and O_2 (99.9999 %). The argon flow was 10 sccm (sccm denotes cubic centimeter per minute at (STP)). D08-2B/ZM gas mass flux controllers (MFC1, MFC2) were used to control the flux of oxygen and argon introduced into the chamber. The sputtering voltage was displayed by a FLUKE 8842 multimeter.

4. RESULTS AND DISCUSSION

Fig. 4 shows the influence of the y position on the distribution of substrate effective area, which is asymmetric. From $Y = -10$ mm, the value of A_s was increased from zero up to a point where the center of the substrate coincide with the center of the target. After the peak, A_s was decreased in steps back down to zero. Obviously, the average area of substrate can be obtained from this theoretical modeling.

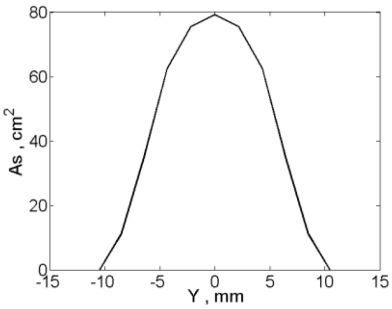


Fig. 4. Calculated effective area of substrate with respect to Y position

From the above modeling, it is possible to calculate the fraction of θ_{t1}, θ_{t2}, θ_{t3}, θ_{t4} as a function of oxygen flow, which was shown in Fig. 5. In reactive sputtering system with a revolutionary substrate, the effective area of substrate is smaller than that of normal system. The values of A_s are chosen as 176 cm^2 and 90.2 cm^2 for normal system and revolutionary system respectively. From the solid lines, it is seen that θ_{t1}, corresponding to the fractional area of the target consisting of metal vanadium, decreases most rapidly for low reactive gas flows, but decreases asymptotically to zero for high flows. In the region up to 2.3 sccm, the fraction of θ_{t4} becomes higher than that of θ_{t2} and θ_{t3}. It is because that the amount of O_2 consumed to VO_2 surpassed the amount of O_2 gettered by deposited V and V_2O_3 at this point, resulting in an increase in the fraction of θ_{t4}. The hysteresis appears when increasing and decreasing the reactive gas flow, which occurs in the region from 4.3 to 4.9 sccm. With the continued increasing amount of oxygen, θ_{t4} increases drastic to 100 %. Meanwhile, the fractions of metal V, V_2O_3 and VO_2 were reduced and eventually disappeared. Similar trends were found in the curves for reactive sputtering system with a revolutionary substrate (dashed line). Compared to the curves obtained by normal system, we clearly see that the calculations predict that the width of S shape of the curves can be decreased for reactive sputtering with a revolutionary substrate. The reduction in hysteresis effect of target coverage which was shown in Fig. 5 is accompanied by the corresponding reduction in hysteresis effect of target voltage.

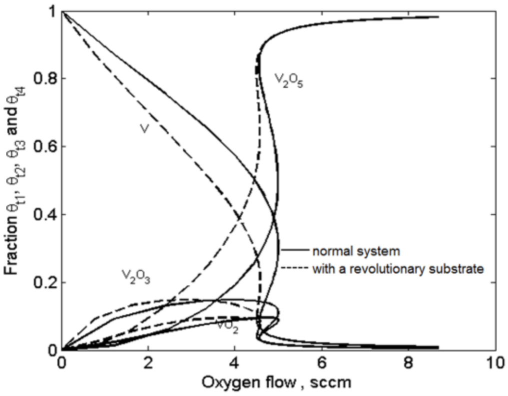
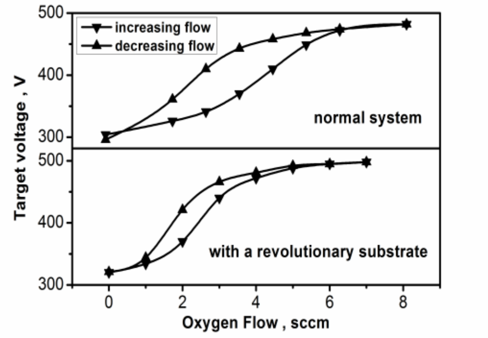
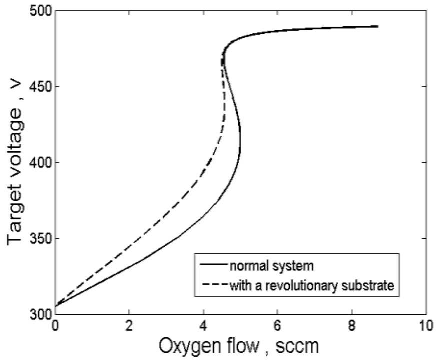


Fig. 5. Calculated results for fraction of θ_{t1}, θ_{t2}, θ_{t3}, θ_{t4} vs supply of the reactive gas for normal reactive sputtering system (solid line) and reactive sputtering system with a revolutionary substrate (dashed line)



a



b

Fig. 6. a – experimental results; b – calculated results of target voltage vs supply of the reactive gas for normal system and system with a revolutionary substrate

The experimental results and modeling results for the target voltage as functions of the reactive gas supply are plotted in Fig. 6.

When comparing the modeling results under two different conditions, it is seen that the calculations predict that the S shape of the curves can be affected and decreased by using a revolutionary substrate. Consequently, it also illustrates the mechanism for eliminating the hysteresis by decreasing the substrate area. Similar trend has been experimentally obtained in Fig. 6 a.

By increasing and decreasing the oxygen supply the expected hysteresis effect appears. As can be seen, there is a pronounced difference in hysteresis width for the curves. Compared with normal system, the curves for reactive sputtering with a revolutionary substrate are shifted toward lower oxygen flows. This behavior may be explained in the following way. The consumption of gas inside the chamber takes place at the target as well as the substrate. However, because the substrate is revolutionary, less reactive gas will be consumed by the receiving area. In conclusion, a revolutionary substrate gives a lower consumption of gas at the substrate, which shifts the hysteresis curves to lower flow values.

5. CONCLUSION

A numerical model for reactive sputtering has been presented where the effect of a revolutionary substrate is taken into account. In this modeling, we assumed metal vanadium and three oxides of V_2O_3, VO_2, and V_2O_5 were formed during reactive sputtering deposition of VO_x. The fraction of V^0, V^{3+}, V^{4+}, V^{5+} (denoted as θ_{t1}, θ_{t2}, θ_{t3}, θ_{t4} here) and target voltage have been investigated as a function of reactive gas flow during the reactive sputtering. From the modeling results, it has been shown that hysteresis effect would be decreased by using a revolutionary substrate because of the significant reduction in substrate effective area.

Experiments were carried out to verify these theoretical findings. Films have been deposited by reactive sputtering using a revolutionary substrate and the normal system, respectively. The curves of target voltage with respect to varied oxygen flow supply were taken under identical processing conditions to those used in the calculations. It is clearly indicated that the hysteresis width from experimental results was also decreased under such condition, strongly support the theoretical predictions. These lead to the conclusion that it is possible to obtain hysteresis-reduced reactive sputtering process by using a revolutionary substrate.

Acknowledgments

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APPENDIX A

The following simulation parameters were used in the work: $\alpha_1 = 1$, $\alpha_2 = 1$, $\alpha_3 = 1$, $Y_{t1} = 0.6$, $Y_{t2} = 0.3$, $Y_{t3} = 0.2$, $Y_{t4} = 0.2$. $l_1 = 3$, $l_2 = 4$, $l_4 = 5$. Target area $A_t = 260$ cm^2, gas temperature $T = 300$ K, pumping speed $S = 0.2$ m^3/s.

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