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TIME-DEPENDENT SIMULATION MODELLING OF REACTIVE SPUTTERING

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A time-dependent simulation model of reactive sputtering is proposed. The model deals with time-dependent poisoning of the target surface and hysteresis phenomena. The model is based on the calculation of the time-dependent change in gettering pumping speed and target poisoning speed, yielding the time-dependent change in target coverage and reactive gas partial pressure. By calculating the equilibrium values of the time-dependent change over a range of reactive gas flow rates, hysteresis effects of target coverage and reactive gas partial pressure are investigated as a function of the gas flow rate. The hysteresis results obtained suggest that with the time-dependent model it is possible to evaluate the effect of pumping speed on the transition points and width of hysteresis curves. As compared with experimentally investigated results it is found that the model explains mechanisms of reactive sputtering qualitively.

1. INTRODUCTION

Reactive sputtering, *i.e.* the removal of surface atoms by energetic particle bombardment in a reactive atmosphere, is an attractive method for preparing compound films such as nitrides or oxides. As the importance of reactive sputtering increases, the mechanisms involved in the process have received considerable attention in connection with the effort to improve process operation and controllability. Since the process includes complex target behaviour, there is still an absence of quantitative understanding of reactive sputtering. Non-linearity, which is observed in the relationship between deposition rate or partial pressure of reactive gas and reactive gas flow rate, is typically the result of the complex behaviour. The process is not affected by the non-linearity when it is operated at the end of the reactive mode. However, the non-linearity causes a reduction in controllability when the process is operated in the transition area between a metallic target surface and an oxidized or nitrided target surface in order to obtain films with an intermediate composition. Both target poisoning and wall gettering are believed to produce non-linearity. At the target surface, as adsorption or incorporation of reactive gas, accompanied by formation of compounds, occurs, the target is poisoned. Simulta-

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neously the compounds formed at the surface are sputtered as a molecular or atomic species. The change in composition of the target surface depends on the relative rates of target poisoning and sputtering. This change is generally expressed as the change in amount of reactive gas on the target:

$$dQ/dt = (dQ/dt)_{ads} + (dQ/dt)_{sp}$$

where $(dQ/dt)_{ads}$ represents the adsorption rate of reactive gas and $(dQ/dt)_{sp}$ the sputtering rate of reactive gas. The value of $(dQ/dt)_{ads}$ is affected by the reactive gas pressure, which is determined by the balance among the introduced, consumed, and pumped-out amounts of gas. Since consumption occurring at the chamber wall surface is due to gettering of the sputtered target metal material, this consumption is strongly correlated to the target surface condition.

The change in the process described above is time dependent. When the sputtering is started with the bare metal target in a reactive atmosphere, the target surface is continuously poisoned until the poisoning and sputtering are balanced; $dQ/dt = 0$. Once the equilibrium is reached, it is kept as long as the sputtering is operated under the same conditions of reactive gas flow rate, sputtering current, and pumping speed. Although understanding of the details of this time-dependent process change is important, not so much interest is paid to the investigation and understanding of the time-dependent process change.

In order to understand physical behaviour, it is helpful to model the process. Moreover, the modelling makes it possible to predict the conditions of process operation. Concerning reactive sputtering, several models have been proposed to explain physical behaviour[1-5]. While most of the models are proposed to explain hysteresis effects investigated in the relationship between deposition rate or reactive gas partial pressure and reactive gas flow rate, few models deal wih the time-dependent change in the target surface. Since, as described above, the hysteresis results from the time-dependent process change, the model needs to be based on the time-dependent change. It is difficult to understand the reactive sputtering process better without this time-dependent calculation.

In this respect the purpose of this paper is to present results of a time-dependent simulation. First several time-dependent simulation results are shown, and then as a result of the time-dependent simulation hysteresis curves are obtained. It should be emphasized that in the time-dependent calculation the process reaches its equilibrium by itself without any assumptions about how the equilibrium between the target surface and the chamber walls is reached.

2. THEORETICAL BASIS

The first step in performing a time-dependent simulation is to understand the behaviour of the reactive gas in the chamber. The flow of reactive gas in the chamber is schematically shown in Fig. 1. Introduced gas is consumed at the target surface and at the chamber wall and pumped out by the vacuum pump system. Simultaneously, adsorbed gas on the target is sputtered. Desorption of the gas gettered at the chamber wall is usually negligible. This relationship is expressed as

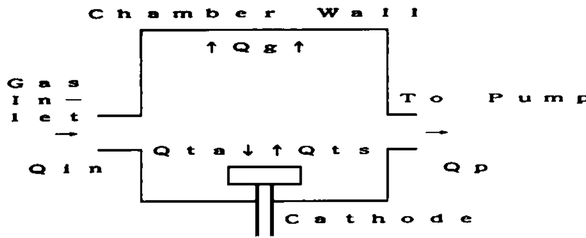

Fig. 1. Schematic drawing of reactive gas flow in the sputtering chamber.

follows:

$$Q_{in} = Q_{ta} - Q_{ts} + Q_g + Q_p \tag{1}$$

where Q_{in} refers to the amount of reactive gas introduced into the chamber, Q_{ta} the amount of adsorbed gas at the target, Q_{ts} the amount of sputtered gas from the target, Q_g the amount of gettered gas at the chamber wall, and Q_p the amount of gas pumped out from the chamber by the vacuum pump system. The adsorption and sputtering at the target surface continue until the target surface behaviour balances. At the equilibrium $Q_{ta} = Q_{ts}$, and thus

$$Q_{in} = Q_g + Q_p \tag{2}$$

In order to express the relationship between Q_{in} and reactive gas partial pessure P, which is assumed to be uniform in the chamber, pumping speeds should be considered. As shown in Fig. 1 it can be assumed that there are four pumps to be considered: target consumption pump, target sputtering source, wall gettering pump, and physical (vacuum) pump. The pumping speeds are defined for each pump: S_{ta} for the target consumption, S_{ts} for the target sputtering, S_g for the wall gettering, and S_p for the vacuum pump. With those pumping speeds eqn. (1) is written as

$$Q_{in} = P(S_{ta} - S_{ts} + S_g + S_p) \tag{3}$$

Those pumping speeds are not measurable during a time-dependent process because they are varying moment by moment while the process is reaching the equilibrium and because S_{ta}, S_{ts} and S_g cannot be measured separately. The measurable change in total pressure is a result of the change in pumping speeds. At the equilibrium, eqn. (3) can be written as

$$Q_{in} = P(S_g + S_p) \tag{4}$$

On the basis of the above discussion, how to express the time-dependent change in the pumping speeds is important. A general method for calculating the change in the process is to deal with the interaction between reactive gas flux and target or chamber wall. In this case the reactive gas flux is determined from the gas kinetics equation, by using the intitial value of the reactive gas pressure (prior to the time at which the glow discharge is turned on, *i.e.* given by $P_0 = Q_{in}/S_p$). However, this is not adequate in the time-dependent simulation because P_0 is not time dependent. In order to bring the time-dependent change in pressure into the simulation it is

necessary to use the relationship given in eqn. (3). Ideally, P would be defined by simulating the interaction between flux and target or chamber wall surface. However, this is impossible because the value calculated from the interaction is not a pumping speed S but the amount of Q of gas, which cannot define P without a definition of S.

In order to avoid this problem, in the simulation S_{ta} and S_g are defined as a function of target coverage θ:

$$S_{ta} = (1-\theta)S_{ta}^0 \tag{5}$$

$$S_g = (1-\theta+\theta Y_{mc}/Y_{mm})S_g^0 \tag{6}$$

where S_{ta}^0 and S_g^0 represent the initial values of S_{ta} and S_g respectively, and Y_{mm} refers to the sputtering yield of metal atoms from the bare target and Y_{mc} the sputtering yield of metal atoms from the poisoned target. The sputtering speed S_{ts} can be derived from θ, sputtering yields, and sputtering current. With this calculation it becomes possible to simulate the time-dependent change.

3. SIMULATION PROGRAM

In the simulation Ti–O_2 reactive sputtering is modelled. There are some assumptions with the simulation model.

(i) At the target one O_2 molecule can be adsorbed by one titanium atom on the surface. The formation of the compounds is not considered. Possible physisorption on the target is also neglected. The reactive gas cannot adsorb onto already poisoned target sites.

(ii) At the chamber wall, similar to phenomena at the target surface, one arriving titanium metal atom can adsorb one O_2 molecule. Gettered gas cannot be desorbed spontaneously. The gettering is regarded as a monolayer phenomenon.

(iii) The physical pumping speed S_p is assumed to be constant for the pressure range simulated.

In the simulation model, first the reactive gas pressure is calculated from the following equation.

$$P = Q_{in}/(S_{ta}+S_g+S_p) \tag{7}$$

The amounts of gas consumed are then calculated:

$$Q_t = PS_{ta} \tag{8}$$

$$Q_g = PS_g \tag{9}$$

If Q_t exceeds the number of available adsorption sites, S_{ta} is reduced to yield a possible Q_{ta}, and then P, Q_t, and Q_g are calculated again. After those calculations, sputtering of the target is dealt with, giving the titanium flux and O_2 flux. The type of the sputtered species is not considered. If the number of titanium atoms sputtered is not large enough to getter all the sputtered O_2 at the wall, then the amount of the excess O_2, is added to Q_{in} at the next calculation step. The target coverage θ, which defines S_{ta} and S_g, is determined from adsorption and sputtering calculations. Then the next step of the calculation is performed with newly obtained values.

4. RESULTS AND DISCUSSION

Typical results of the time-dependent simulation for two different O_2 flow rates F_{O_2} are shown in Figs. 2 and 3. The initial pumping speeds are $S_p = 150 \mathrm{l\,s^{-1}}$, $S_{ta}^0 = 10 \mathrm{l\,s^{-1}}$, and $S_g^0 = 300 \mathrm{l\,s^{-1}}$. The sputtering current I_{sp} is 2 A. The sputtering yield Y_{mm} of titanium atoms from the bare titanium target is assumed to be 0.32, that Y_{mc} of titanium atoms from the poisoned target is assumed to be 0.015, and that Y_{gc} of O_2 atoms from the poisoned target is assumed to be 0.015. The target is not poisoned at the beginning of the calculaton: $\theta^0 = 0$.

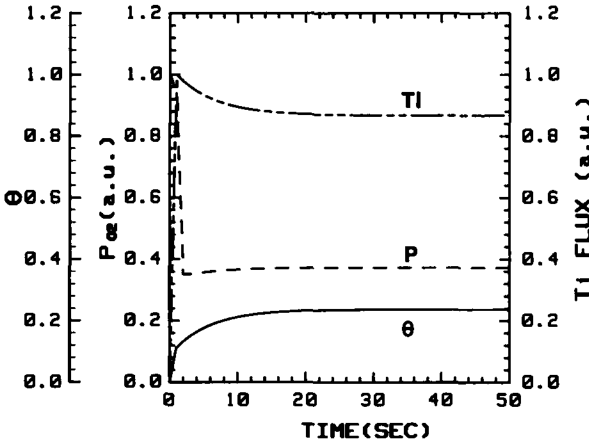

Fig. 2. Simulation results of the time-dependent change: $F_{O_2} = 4$ standard cm^3 min^{-1}, $S_p = 150 \mathrm{l\,s^{-1}}$, $S_g^0 = 300 \mathrm{l\,s^{-1}}$, $S_{ta}^0 = 10 \mathrm{l\,s^{-1}}$, $I_{sp} = 2$ A, $\theta^0 = 0$.

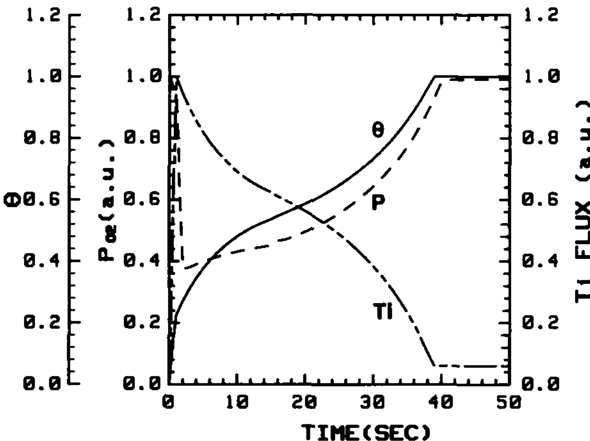

Fig. 3. Simulation results of the time-dependent change: $F_{O_2} = 8$ standard cm^3 min^{-1}, $S_p = 150 \mathrm{l\,s^{-1}}$, $S_g^0 = 300 \mathrm{l\,s^{-1}}$, $S_{ta}^0 = 10 \mathrm{l\,s^{-1}}$, $I_{sp} = 2$ A, $\theta^0 = 0$.

At the first stage of the simulation it is shown that a non-poisoned target yields a large titanium flux, which can getter the reactive gas, reducing pressure. As the target is poisoned, the gettering capacity decreases, resulting in an increase in O_2

pressure. At $F_{O_2} = 4$ standard cm^3 min^{-1} the final value of θ is 0.24, indicating that the target has not been completely poisoned. At $F_{O_2} = 8$ standard cm^3 min^{-1} there is a change in poisoning rate before the steady state is reached, and the curves do not exhibit rounding, especially at the end of the poisoning. The time to reach equilibrium is shorter at $F_{O_2} = 4$ standard cm^3 min^{-1} than $F_{O_2} = 8$ standard cm^3 min^{-1}. The final θ at $F_{O_2} = 8$ standard cm^3 min^{-1} is 1.0; the target is completely poisoned.

In Fig. 4 results obtained for the calculation starting with the target poisoned *i.e.*, $\theta^0 = 1$, are shown. The value of F_{O_2} is 2 standard cm^3 min^{-1}. In this case the compound on the target is continuously sputtered, resulting in the decrease in θ. A final value of 0.11 is found. When F_{O_2} is large enough to keep poisoning the target surface there is no change in θ.

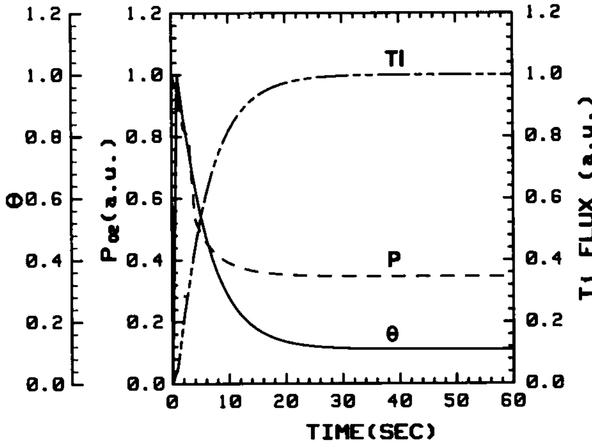

Fig. 4. Simulation results of the time-dependent change: $F_{O_2} = 2$ standard cm^3 min^{-1}, $S_p = 150$ l s^{-1}, $S_g^0 = 300$ l s^{-1}, $S_{ta}^0 = 10$ l s^{-1}, $I_{sp} = 2$ A, $\theta^0 = 1$.

A hysteresis curve was drawn by calculating the equilibrium values over a range of F_{O_2} between 0 and 10 standard cm^2 min^{-1} with F_{O_2} varying in steps of 0.5 SCCM. When F_{O_2} was increased to 10 standard cm^3 min^{-1}, $\theta^0 = 0$, and when F_{O_2} was decreased to 0 standard cm^3 min^{-1}, $\theta^0 = 1$. Calculated results for $S_p = 150$ l s^{-1} are shown in Fig. 5. When F_{O_2} increases to 8 standard cm^3 min^{-1} an avalanche change occurs. This is the transition from reactive mode to non-reactive mode. After the transition θ is unity and P_{O_2} increases linearly. When F_{O_2} decreases the onset of the reverse transition takes place at $F_{O_2} = 7$ standard cm^3 min^{-1}, yielding a hysteresis width of 1 standard cm^3 min^{-1}. After the reverse transition the sputtering of the compound on the target is dominant. Thus θ decreases as F_{O_2} decreases. At $S_p = 50$ l s^{-1}, the transition points move to 5.5 standard cm^3 min^{-1} and 2.5 standard cm^3, min^{-1}, widening the hysteresis to 2.5 standard cm^3 min^{-1}, as shown in Fig. 6. Results for two values of S_p show that the model can simulate the hysteresis and can estimate effects of the pumping speed on the hysteresis curves.

In order to compare the simulation results with experimentally measured results hysteresis behaviour was investigated in Ti–O_2 reactive sputtering. Figure 7

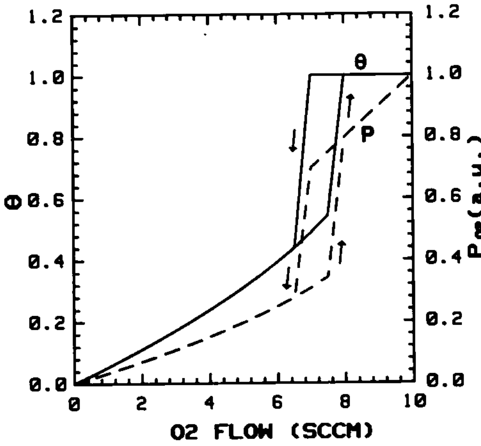

Fig. 5. Calculated hysteresis curves: $S_p = 150 \mathrm{l\,s^{-1}}$, $S_g^0 = 300 \mathrm{l\,s^{-1}}$, $S_{ta}^0 = 10 \mathrm{l\,s^{-1}}$, $I_{sp} = 2$ A.

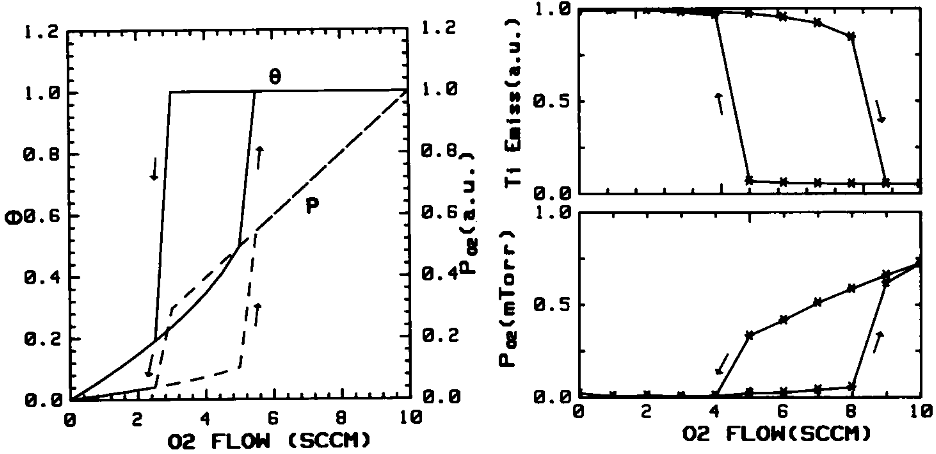

Fig. 6. Calculated hysteresis curves: $S_p = 50 \mathrm{l\,s^{-1}}$, $S_g^0 = 300 \mathrm{l\,s^{-1}}$, $S_{ta}^0 = 10 \mathrm{l\,s^{-1}}$, $I_{sp} = 2$ A.

Fig. 7. Experimentally obtained titanium emission intensity and O_2 gas partial pressure curves as a function of O_2 flow rate: $S_p = 150 \mathrm{l\,s^{-1}}$, $I_{sp} = 2$ A.

shows experimentally observed hysteresis curves of titanium emission intensity I_{Ti} and oxygen partial pressure P_{O_2}. The sputtering current was kept at 2 A, and S_P was $220 \mathrm{l\,s^{-1}}$. After an equilibrium was reached, F_{O_2} was increased or decreased by 1.0 standard $\mathrm{cm^3\,min^{-1}}$. An avalanche change in both I_{Ti} and P_{O_2} occurs when F_{O_2} exceeds 8 standard $\mathrm{cm^3\,min^{-1}}$. Before the transition, most of the O_2 is consumed. Thus P_{O_2} is nearly equal to 0. After the transition I_{Ti} drops to 1/20 of the initial value. The transition from non-reactive to reactive mode occurs between $F_{O_2} = 5$ standard $\mathrm{cm^3\,min^{-1}}$ and $F_{O_2} = 4$ standard $\mathrm{cm^3\,min^{-1}}$. After the second transition, I_{Ti} and P_{O_2} trace the previously obtained lines.

Those experimentally observed results agree qualitatively with the calculated result. Since the pumping speeds and sputtering yields which are used in the simulation model cannot be estimated correctly, there exists a discrepancy between

experimental and calculated values. By optimizing those values it is possible to fit a calculated curve to an experimentally observed curve. This is, however, not thought to be very meaningful. It is necessary to evaluate the pumping speeds and sputtering yields more accurately in order to perform quantitative simulation. More detailed studies of the simulation model will be carried out.

5. CONCLUSIONS

A simulation model which explains time-dependent change in reactive sputtering is proposed. The model is based on the calculation of the time-dependent change in gettering pumping speed, target poisoning speed, and reactive gas pressure. The equilibrium is reached by giving initial conditions, without assuming anything about how the equilibrium is reached. Calculation of the equilibrium values over a range of reactive gas flow rates yields hysteresis curves of target coverage and reactive gas pressure. The width and transition points vary with pumping speeds. Although the calculated results do not agree perfectly with experimental results, it is believed that the simulation model explains qualitatively the mechanism of the time-dependent change in reactive sputtering.

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