PLASMA KINETIC MODEL OF DC MAGNETRON REACTIVE SPUTTERING IN AR - O_2 GAS MIXTURES

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A model of reactive sputtering, which includes plasma chemistry for the first time in DC magnetron discharges, has been developed. Argon and oxygen have been chosen as buffer and reactive gases, respectively, and silicon as the target material. Sputtering by oxygen ions is included in the model. The model allows the investigation of the sputtering process and the plasma chemistry of the discharge for an arbitrary ratio of partial pressures of reactive and buffer gases.

I. INTRODUCTION

A number of analytical models of reactive sputtering have been developed so far (see, for example, [1] and referents therein). These models reflect major features of the reactive sputtering process such as hysteresis, effects of pump speed, substrate and target areas, and ion current. However, none of these models consider the plasma chemistry of the glow discharge. To get agreement with experiments, these models assume a sticking coefficient of the reactive gas to the metal target equal to 1 for all the reactive gas in the chamber. This assumption, however, is not very accurate, because the original reactive gas has a much smaller sticking coefficient than the species created in the discharge. For example, it is about 0.01 for molecular oxygen on a silicon surface [2], while the sticking coefficient for atomic oxygen is close to 1.

In this work we developed a model of DC magnetron reactive sputtering, which takes into account the plasma chemistry of the discharge. We have calculated the rate coefficients of plasma chemical reactions and solved the plasma chemistry equations together with the sputtering deposition equations. Generally, deposition of any oxide film can be studied with the model presented here, in this work we will consider sputtering of an Si target as an example.

II. BASIC EQUATIONS.

The "sputtering" part of our model uses the same idea of reactive particle conservation previously developed by Berg et. al. [3]. In our model, however, we have included additional terms due to sputtering by oxygen ions, target and substrate oxidation by atomic oxygen and target oxidation by oxygen ions. As in previous models, all characteristics are considered as averaged over the cathode and substrate areas.

Thus, the fluxes of sputtered silicon and oxygen atoms from the target are

$$I_{Si}^{sp} = J_{Ar} Y_{Si}^{Ar} (1-\theta^t E_{Ar}) + J_{O2} Y_{Si}^{O2} (1-\theta^t E_{O2}) + J_O Y_{Si}^{O} (1-\theta^t E_O) \ , \quad (1)$$

$$I_O^{sp} = (J_{Ar} Y_O^{Ar} + J_{O2} Y_O^{O2} + J_O Y_O^{O})\theta^t \ , \quad (2)$$

where indices Ar, O, and O2 correspond to argon, atomic, and molecular oxygen; J is the flux of the corresponding sort of ions; I_{Si}^{sp} and I_O^{sp} are the fluxes of sputtered silicon and oxygen atoms from the target correspondingly; θ^t is the target stoichiometry ($\theta^t = 0$ for pure silicon, and $\theta^t = 1$ for SiO_2 film); Y_{Si}^{p} and Y_O^{p} (p = Ar, O2 or O) are the silicon sputtering yield for pure silicon target and the oxygen sputtering yield for a completely oxidized target, respectively, by p ions. Here we have assumed that: 1) sputtering yields are linear functions of target stoichiometry θ^t; 2) for a film with $\theta^t = 1$ we have the silicon sputtering yields as $Y_{Si}^{p} (1 - E_p)$. Note, that the target erosion is determined by the sputtering rate of silicon.

The flux of oxygen atoms sticking to the cathode, I_O^t, can be written as:

$$I_O^t = (2\,\alpha_{O2}^t F_{O2} + \alpha_O^t F_O + 2\,\alpha_{JO2}^t J_{O2} + \alpha_{JO}^t J_O)(1-\theta^t) \ , \quad (3)$$

$$F_{O2} = \frac{1}{4} n_{O2} V_{O2} \ , \quad (3a) \qquad F_O = \frac{1}{4} n_O V_O \ , \quad (3b)$$

Here $\alpha_p{}^t$ is the sticking coefficient of the particles of type p to the pure silicon target surface; F_{O2} and F_O are the fluxes of molecular and atomic oxygen to the target, respectively. They are expressed through the average number densities n_{O2} and n_O in the chamber volume and the thermal speeds V_{O2} and V_O.

The oxygen flux onto the target surface should be equal to the flux of oxygen being removed from the cathode by sputtering:

$$I_O{}^t = I_O{}^{sp} \quad . \tag{4}$$

The flux $I_{Si}{}^s$ of sputtered silicon on the substrate is determined by the flux of silicon atoms sputtered from the target and relative areas of the target A^t and the substrate A^s:

$$I_{Si}{}^s = I_{Si}{}^{sp}\ A^t/A^s. \tag{5}$$

For the substrate area we assume, as it was done in [3], the total area (including the substrate and walls of the vacuum chamber), where the deposition takes place. The flux of oxygen gettering to the substrate, $I_O{}^s$, is determined by the sputtered oxygen flux from the target plus the flux of oxygen molecules and atoms from the plasma:

$$I_O{}^s = (\alpha_O{}^s I_O{}^{sp}\frac{A^t}{A^s} + 2\,\alpha_{O2}{}^s F_{O2} + \alpha_O{}^s F_O)\,(1 - \theta^s) \quad , \tag{6}$$

$$I_O{}^s / I_{Si}{}^s = 2\,\theta^s \quad . \tag{7}$$

Here $\alpha_O{}^s$ and $\alpha_{O2}{}^s$ are the sticking probabilities of atomic and molecular oxygen to the pure silicon substrate respectively, and θ^s is the substrate stoichiometry. We neglect in Eq. (6) the collisions of sputtered oxygen atoms with electrons during their travel to the substrate. This assumption is correct when the free path length for sputtered atoms exceeds the distance between the target and the substrate. For optical applications this assumption is usually well satisfied.

The total discharge current density, J^t, is determined by the total flux of all types of ions. Assuming that the coefficient of ion bombardment induced secondary electron emission is small, J^t is given by:

$$J^t = e\,(J_O + J_{O2} + J_{Ar}) \quad , \tag{8}$$

where e is the magnitude of the charge of an electron.

For the plasma chemistry of the glow discharge we have considered the following reactions :

$$O_2 + e \rightarrow O + O^+ + e \qquad k_1 = 1.8\ 10^{-8}\ cm^3/s \tag{r1}$$

$$O_2 + e \rightarrow O_2^+ + e + e \qquad k_2 = 4.7\ 10^{-8}\ cm^3/s \tag{r2}$$

$$O_2 + e \rightarrow O + O + e \qquad k_3 = 2.0\ 10^{-8}\ cm^3/s \tag{r3}$$

$$O + e \rightarrow O^+ + e + e \qquad k_4 = 3.6\ 10^{-8}\ cm^3/s \tag{r4}$$

$$Ar + e \rightarrow Ar^+ + e + e \qquad k_5 = 8.0\ 10^{-8}\ cm^3/s \tag{r5}$$

$$Ar + e \rightarrow Ar^* + e \rightarrow Ar^m + e + h\nu \qquad k_6 = 3{,}7\ 10^{-9}\ cm^3/s \tag{r6}$$

$$Ar^m + e \rightarrow Ar^+ + e + e \qquad k_7 = 1.4\ 10^{-7}\ cm^3/s \tag{r7}$$

$$Ar^m + e \rightarrow Ar^* + e \rightarrow Ar + e + h\nu \qquad k_8 = 1.9\ 10^{-9}\ cm^3/s \tag{r8}$$

$$Ar^m + Ar^m \rightarrow Ar^+ + Ar + e \qquad k_8 = 1.9\ 10^{-9}\ cm^3/s \tag{r9}$$

The rate constants for reactions (r1) - (r8) have been calculated using the cross sections from [4-6]. A low pressure DC magnetron discharge usually exhibits a highly non-Boltzman electron energy distribution function (see, for example, in [7]. Therefore, we have calculated the rate coefficients for these reactions using specially developed propagator model. The model calculates the collision probabilities for an electron moving in crossed E x B fields in this region. The values of rate coefficients have been calculated for the electrical field E = 400 V/cm and the magnetic field B = 200 G, which are typical for DC magnetron discharges. The details of our propagator model will be published elsewhere. The rate coefficient for reaction (r9) has been taken from [8].

Now, the equations for the ion fluxes can be written as:

$$J_{Ar}\,A^t = k_5\,n_{Ar}\,n_e\,A^t\,d + k_7\,n_{Ar^*}\,n_e\,A^t\,d + k_9\,n_{Ar^*}\,n_{Ar^*}\,V \ , \tag{9}$$

$$J_{O2}\,A^t = k_2\,n_{O2}\,n_e\,A^t\,d \ , \tag{10}$$

$$J_O\,A^t = (k_1\,n_{O2} + k_4\,n_O)\,n_e\,A^t\,d \ , \tag{11}$$

where J is the total ion flux; d is the thickness of the near cathode bright region; n_e is the average electron density over this region; n_{Ar^m} is the average metastable excited argon density over the total plasma volume V; n_{Ar} is the number density of ground state argon. Equations (9) - (11) assume that all the ions created in the plasma go to the target without any other collisions. This is valid, because the ion free path length is bigger than d. Also, Eq. (9) assumes that the metastable argon atoms are distributed homogeneously over the total plasma volume .

Kinetic equations for molecular oxygen, atomic oxygen, argon, and metastable argon can now be written as:

$$Q_{O2} = (k_1 + k_2 + k_3)\, n_{O2}\, n_e\, A^t d + n_{O2}\, S_{O2} + \\ + F_{O2}\, A^t \alpha_{O2}{}^t (1 - \theta^t) + F_{O2}\, A^s \alpha_{O2}{}^s (1 - \theta^s) \quad , \qquad (12)$$

$$(2\,k_3 + k_1)\, n_{O2}\, n_e\, A^t d + 2\, J_{O2}\, [1 - \alpha_{JO2}{}^t (1 - \theta^t)\,]\, A^t + \\ J_O\, [1 - \alpha_{JO}{}^t (1 - \theta^t)\,]\, A^t + I_O{}^{sp} A^t\, [1 - \alpha_O{}^s (1 - \theta^s)\,] = n_O\, S_O + \\ + F_O\, \alpha_O{}^t (1 - \theta^t)\, A^t + F_O\, \alpha_O{}^s (1 - \theta^s)\, A^s + k_4\, n_O\, n_e\, A^t d \;\; , \quad (13)$$

$$Q_{Ar} = n_{Ar}\, S_{Ar} + n_{Ar^m}\, S_{Ar^m} \quad , \qquad (14)$$

$$k_6\, n_{Ar}\, n_e\, A^t d = (k_7 + k_8)\, n_{Ar^m}\, n_e\, A^t d + \\ + 2\, k_9\, n_{Ar^m}\, n_{Ar^m}\, V + n_{Ar^m}\, S_{Ar^m} \quad , \qquad (15)$$

where the left hand parts of these equations describe the productions and the right hand parts describe the losses for molecular oxygen, atomic oxygen, ground state argon, and metastable argon correspondingly. Q_{O2} and Q_{Ar} are the flow rates for molecular oxygen and argon respectively; S_{Ar}, S_{O2}, S_O, and S_{Ar^m} are the pump speeds for argon, molecular oxygen atomic oxygen, and metastable argon respectively.

Note that in the model we have separately considered the low energy oxygen atoms (their flux is F_O), and the high energy sputtered oxygen atoms (their flux is $I_O{}^{sp}$). This has been done to take into account that the high energy oxygen neutrals do not participate in chemical reactions because they reach the substrate without collisions, while the low energy oxygen atoms undergo many collisions with electrons in the plasma region before they reach the target or the substrate. This assumption is valid when the travel time for energetic neutrals to the substrate is less then their average collision time with electrons that is well satisfied in our conditions. It has been also assumed that all the oxygen atoms reflected from the target or the substrate, have low energy.

III. NUMERICAL RESULTS AND CONCLUSIONS

For numerical calculations we have used the following data:

$Y_{Si}^{Ar} = 0.36$, $Y_{Si}^{O2} = 0.4$, $Y_{Si}^{O} = 0.3$, $Y_{O}^{Ar} = 0.36$, $Y_{O}^{O2} = 0.45$, $Y_{O}^{O} = 0.38$; $E_{O2} = E_{Ar} = E_{O} = 0.67$; $\alpha_{O2}^{t} = \alpha_{O2}^{s} = 0.01$, $\alpha_{O}^{t} = \alpha_{JO2}^{t} = \alpha_{JO}^{t} = \alpha_{O}^{s} = 1$; $A^{t} = 250\ cm^2$, $A^{s} = 2500\ cm^2$, $d = 1\ cm$, $L = 5\ cm$, $V = L\ A^{s} = 12500\ cm^3$.

The sputtering yield of silicon atoms by argon ions have been taken from [9]. All other sputtering yields were assumed based on the model [10]. The sticking probability of molecular oxygen to the silicon surface was taken from [2].

The main results of our numerical calculation, for different pump speeds, gas pressures, and mixtures are the following.

1. The main oxidizer of both the target and the substrate oxidizer is atomic oxygen, created in the plasma. The contribution of target poisoning from molecular oxygen, as well as oxygen ions is rather small.

2. The target erosion in the studied region is approximately proportional to the current. High pump speed increases the erosion rate slightly. Argon ions carry the main part of the total current. The contribution of molecular and atomic oxygen ions reaches up to 20% of the total current.

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