Modeling of the target surface modification by reactive ion implantation during magnetron sputtering

D. Depla
Department of Solid State Sciences, University of Ghent, Krijgslaan 281 (S1), B-9000 Ghent, Belgium

Z. Y. Chen, A. Bogaerts, and V. Ignatova
Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk-Antwerpen, Belgium

R. De Gryse
Department of Solid State Sciences, University of Ghent, Krijgslaan 281 (S1), B-9000 Ghent, Belgium

R. Gijbels
Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk-Antwerpen, Belgium

(Received 15 October 2003; accepted 22 December 2004; published 20 July 2004)

The erosion rate of an aluminum target bombarded with Ar$^+$ and O$_2^+$ ions was simulated using TRIDYN. An abrupt change of the erosion rate is noticed at a critical mole fraction of O$_2^+$ ions. This target behavior can also be described by a simple analytical model showing that the abrupt change finds its origin in an avalanche induced by reaction ion implantation. Indeed, by the reduction of the average sputter yield by compound formation, more reactive ions become implanted into the target as the number of implanted ions depends inversely on the average sputter yield. As such, an avalanche situation can develop which finally results in a completely oxidized target. It is also shown that the critical mole fraction depends linearly on the sputter yield of the target material and that target poisoning induced by ion implantation can result in a hysteresis behavior for the target condition. © 2004 American Vacuum Society. [DOI: 10.1116/1.1705641]

I. INTRODUCTION

During reactive magnetron sputter deposition of oxides, nitrides, carbides, and other compounds, abrupt changes in deposition rate, target voltage, and reactive gas pressure have been noticed by several authors. Several models have been formulated to explain these avalanche-like changes. They describe the dynamic balance between compound formation on the target surface and the compound dissociation by the sputtering process as a function of the reactive gas flow. Under conditions of high pumping speed and low current, these models predict no avalanche-like changes. However, it was shown recently that during reactive sputtering of Si$_3$N$_4$, under conditions of high pumping speed and low current, the target voltage changes abruptly at a given critical mole fraction. This effect and other experimental results can be explained by a mechanism based on the reactive ion implantation during the magnetron sputter process. The implantation of reactive ions results in the subsurface formation of the compound, which has a lower sputter yield than the original target material. The chemical reaction between the implanted atoms and the target material results therefore in a decrease of the target surface erosion speed, and consequently the surface concentration of the implanted species, which is inversely proportional to the erosion speed, increases, further reducing the erosion speed of the target surface. This mechanism can result in an avalanche-like change of the target surface condition. Recently, the authors have studied this mechanism in detail, using a dynamic Monte Carlo model. The simulation code TRIDYN was applied to simulate the bombardment of Ar$^+$ and O$_2^+$ ions on an aluminum target and to investigate the reactive sputtering of aluminum in a magnetron discharge. It was shown that the formation of aluminum oxide always takes first place in the subsurface region. Moreover, we have investigated the calculated erosion rate as a function of the oxygen mole fraction. Besides the expected decrease of the erosion rate, we found an abrupt change in the erosion rate at a mole fraction $f = 0.03$. These numerical results confirm the proposed idea of target poisoning by reactive ion implantation.

In this article, we have used the same simulation code TRIDYN to study this abrupt change of the erosion rate in more detail. We compare the results of these simulations with an analytical model. A first version of this analytical model was used to describe the effect of ion implantation on the target condition during reactive magnetron sputtering. The aim of this article is to verify the validity of this analytical model by comparison with the TRIDYN results.

II. DESCRIPTION OF THE TRIDYN SIMULATIONS

The TRIDYN simulations were described in detail. The effective surface binding energy of Al and O was chosen in dependence on the actual surface composition by use of a matrix method as described by Möller et al. Because the incident energy of the reactive ions O$_2^+$ is very high compared to the dissociation energy of the oxygen molecule, surface collision will cause an immediate dissociation of O$_2^+$. Therefore, TRIDYN uses half of the incident energy of O$_2^+$ as the incident energy of the O$^+$ ions but its fluence is doubled. In these simulations we assume no formation of oxygen molecules in the target and the extra oxygen over the

---

*Electronic mail: diederik.depla@UGent.be*
stoichiometry will outdiffuse from the target. A proper fluence increment of $10^{12}$ ions/pseudoparticle is used, which is a good choice to reduce computer time and to maintain precision. The total applied fluence was chosen to reach steady-state conditions. For convenience of description, let $f$ denote the ratio of the pseudoparticle number of $O_2^-$ ions to the sum of $Ar^+$ and $O_2^-$ ions. Assuming that the ratio of $Ar^+$ and $O_2^-$ fluxes is proportional to the ratio of the partial pressure of Ar and $O_2$, the $f$ is identical to the oxygen mole fraction in the plasma. We realize that chemisorption of the reactive gas on the target and the gettering of the reactive gas by the sputtered Al atoms will also influence the behavior of the reactive sputtering process. However, the goal of this simulation is to study the effect of ion implantation on the target condition during reactive magnetron sputtering. Therefore, we assume that the oxygen mole fraction in the plasma is known and we neglect the impingement of other species (i.e., $O_2$, $Ar$, $O_2$, and $O$) than $Ar^+$ and $O_2^-$ on the target surface. At this point we wish to mention that several processes which can occur during ion implantation and sputtering are not included in this TRIDYN code, e.g., Gibbsian segregation, radiation-enhanced diffusion, recoil implantation, and others. These processes can have an influence on the oxidation mechanism. However, as stated before, the aim of this article is a comparison between the results of this TRIDYN code and a simple analytical model, which also does not include these effects.

III. RESULTS AND DISCUSSION

A. TRIDYN simulations

The TRIDYN code was used to simulate the bombardment of aluminum by $Ar^+$ and $O_2^-$ ions. For different oxygen mole fractions $f$, we have calculated the surface erosion due to this ion bombardment as a function of the fluence. From such a simulation, the steady-state erosion rate was calculated and its change studied as a function of the oxygen mole fraction. We have performed such a simulation at four different energies, i.e., 180, 360, 720, and 1440 eV. We realize that the simulations performed at high ion energy (720 and 1440 eV) represent less realistic magnetron sputtering conditions because, generally speaking, the ion energy during dc magnetron sputtering is of the order of 400 eV. We have used a much wider energy interval to study the influence of reactive ion implantation on the target condition in a more general way. The simulation results, i.e., the erosion rate as a function of the oxygen mole fraction, are presented in Fig. 1.

Due to the compound formation, which reduces the average sputter yield of the target, we notice an overall decrease of the erosion rate as a function of the oxygen mole fraction. However, at a given critical mole fraction $f_{cr}$, we notice an abrupt change for the erosion rate. The abrupt drop is for the lowest energy only 1% of the erosion rate in metallic mode ($f = 0.0$) while at high energy we notice a drop of $\sim 10$%. This abrupt change of the erosion rate occurs in a very narrow reactive mole fraction interval (interval width $\Delta f$ equals $5 \times 10^{-4}$ for the lowest energy and $1 \times 10^{-3}$ for the highest energy). These results seem to confirm the proposed mechanism for the avalanche-like change of the target condition under influence of reactive ion implantation. A similar result was obtained with a version of an analytical model. Meanwhile we have further improved this analytical model, and in the following, this model is described and its results compared with the TRIDYN results. In this way, we wish to verify the validity of this analytical model.

B. Analytical model: First version

At a given reactive gas mole fraction $f$, the steady state target condition can be described as a target composed of two materials having a strongly different sputter yield, i.e., the original target material with sputter yield $\gamma_M$ and the compound formed by reactive ion implantation with sputter yield $\gamma_c$. Similar to the sputtering of alloys, the target can be divided into a subsurface ($b$) and a surface ($s$) region with a different composition due to the difference in sputter yield of the two components. Of course, below these two defined regions the unaffected bulk target material is found. For both regions, i.e., the subsurface and surface region, we can define a degree of target reaction $\theta$, which refers to mole fraction of compound $MR_c$ in this region. The relation between the degree of target reaction for the subsurface region $\theta_b$ and the surface region $\theta_s$ can be described similar to the sputtering of alloys. In steady state, the amount of compound coming into the surface layer is $\theta_s v_s$ with $v_s$ the erosion rate, defined as $[(1 - \theta_s) \gamma_M + \theta_s \gamma_c](I)/n_{os}$, while the compound is removed from the surface at a rate equal to $\gamma_c \theta_s I$, with $I$ the ion current density and $n_{os}$ the target density. So the net rate of change for the compound in the surface layers is given by

$$n_{os} \frac{d\theta_s}{dt} = n_{os} \theta_s v_s - \gamma_c \theta_s I,$$

with $n_{os}$ the target surface density (atoms/cm$^2$).

From Eq. (1), it follows that at steady state:
The steady state erosion rate can then be calculated as

$$\frac{\gamma_c \theta_s}{\gamma_M (1-\theta_s)} = \frac{\theta_b}{1 - \theta_b}. \quad (2)$$

The steady state erosion rate can then be calculated as

$$v_s = \left( \frac{1 - \theta_b}{\gamma_M + \gamma_c \gamma_b} \right)^{\frac{1}{n_0}}. \quad (3)$$

In steady state, the compound formation by reactive ion implantation must compensate the compound sputter removal. In order to describe this process, we must consider not only the surface region $s$ and the subsurface region $b$, but also a third region $r$ where the reactive ions become implanted and can react with the target material. As shown in Fig. 2, also a third region $r$ where the reactive ions become implanted and can react with the target material.

In steady state the compound formation by reactive ion implantation can be described as follows. The erosion of the target over a distance $\Delta s = v_s \Delta t$ results in a material transfer from the subsurface region $b$ towards the surface region $s$. The ion bombardment of the substrate causing this target erosion results in the implantation of reactive ions into a layer with a thickness equal to $v_s \Delta t$. The implanted ions can react with the target material to form a layer with a composition equal to the subsurface layer, i.e., the compound mole fraction must be equal to $\theta_b$. Therefore, to describe this process we can consider only the subsurface region and represent this region by a two-dimensional matrix $M$. To remove one monolayer of this region, we must bombard the target with $A (1 + z \theta_b) / \gamma_b$ ions, with $A$ the number of rows in the two-dimensional matrix $M$ and $\gamma_b$ the average sputter yield in the subsurface region. The term $(1 + z \theta_b)$ accounts for the increase in density due to the compound formation. Indeed, by the ion implantation the number of atoms to be sputtered increases so, $z$ represents the number of $R$ atoms needed to form the compound molecule $MR$. If $f$ represents the mole fraction of reactive ions in the plasma, $2fA (1 + z \theta_b) / \gamma_b$ reactive atoms $R$ become implanted in the target. Neglecting the implantation profile, we can assume that the $R$ atoms become implanted in one column of the two-dimensional matrix $M$. These $R$ atoms will react with the target atoms, which is represented in this model by setting the value of $N_{i,j} = 1$, where $i$ is randomly chosen for each implanted atom. As a target atom cannot react a second time with an implanted $R$ atom the value of $N_{i,j}$ can only be 0 or 1, i.e., we assume that the $R$ atom is lost for the chemical reaction if it encounters a matrix element $N_{i,j} = 1$. After implantation of $2fA (1 + z \theta_b) / \gamma_b$ reactive atoms, we remove the first monolayer of the target, which is represented in this model by $N_{i,j + 1} = 1$. In this way, the implanted $R$ atoms are shifted towards the target surface, where they modify the sputter yield, i.e., the sputter yield can be described as

$$\gamma_b = \gamma_M + (\gamma_c - \gamma_M) \theta_b$$

with

$$\theta_b = 1/A \sum_{j=1}^{A} N_{i,j}, \quad (4)$$

with $\gamma_M$ the sputter yield of the metal and $\gamma_c (< \gamma_M)$ the sputter yield of the compound. Using the new value for the sputter yield $\gamma_b$ we calculate again the number of reactive $R$ atoms and the implantation process is repeated until the fraction $\theta_b$ of reacted target atoms in the first monolayer remains constant. Figure 3(a) (open symbols) shows the results of such a calculation using $\gamma_M = 0.5$, $\gamma_c = 0.05$, and $z = 1$. We clearly notice the abrupt change of the target condition at a critical mole fraction $f_{cr} = 0.065$.

For a further evaluation of this mechanism, we can describe the above-mentioned simple model more analytically. In steady state the amount of compound formed and removed should be equal. Or

$$\dot{F} = \dot{R}, \quad (5)$$

where $\dot{F}$ and $\dot{R}$ denote the formation and removal rate.

At steady state the first monolayer of the subsurface region contains in our simple model, $A \theta_b$ compound molecules. The time needed to remove this first monolayer depends on the erosion rate $v_s$, which is equal to $I \gamma_s / A$ with
From Eq. $\sim5$ the target reduces the reaction probability for the next incoming atom. This can be expressed as

$$g\frac{d\theta_b}{dn} = \frac{\alpha}{zA}(1 - \theta_b),$$

(7)

with $\alpha$ the probability for reaction between $R$ and a target atom and $z$ the number of $R$ atoms needed to form the compound molecule $MR_z$. The total number of implanted atoms per removed monolayer corresponds with $2fA(1 + z\theta_b)/\gamma_b$, which becomes implanted in a time interval $A/\gamma_I$.

Therefore, the formation rate $F$ equals

$$F = \gamma_I(1 - e^{-[(a/z)f(1+z\theta_b)/\gamma_I]}).$$

(8)

Combining Eq. (8) with Eqs. (5) and (6) results in an equation relating $\theta_b$ with $f$:

$$- \frac{z}{2\alpha}\ln(1 - \theta_b)[(\gamma_M + \theta_b(\gamma_e - \gamma_M)] = f.$$  

(9)

Choosing a value for $\theta_b$ the corresponding mole fraction $f$ can be calculated and, as shown in Fig. 3(a) (solid line), this equation describes the simple model correctly. Using Eqs. (2) and (3), one can calculate from the value of $\theta_b$, the surface composition $\theta_s$ [Fig. 3(b)] and the yield (or erosion rate $v_s$) [Fig. 3(c)].

As shown in Fig. 3(c), the behavior of the yield (or erosion rate) as a function of the mole fraction calculated from this analytical model is very similar to the results from the TRIDYN simulations. Using the sputter yields for both $\text{Al}_2\text{O}_3$ and $\text{Al}$ calculated with the TRIDYN code, setting $z = 1.5(\text{Al}_2\text{O}_3)$ and $\alpha = 1$, we can compare the results from this analytical model with the TRIDYN results. Such a comparison (see Table I) shows that the analytical model predicts larger values for the critical mole fraction than the TRIDYN simulations.

### Table I. Comparison of the critical mole fraction $f_{cr}$ for the $\text{Al}/\text{O}_2/\text{Ar}$ reactive sputtering system simulated with TRIDYN and calculated from the analytical model.

<table>
<thead>
<tr>
<th>Ion energy (eV)</th>
<th>$f_{cr,\text{TRIDYN}}$</th>
<th>$f_{cr,\text{analytical}}$ [Eq. (9)]</th>
<th>$f_{cr,\text{analytical}}$ [Eq. (10)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>0.018</td>
<td>0.042</td>
<td>0.019</td>
</tr>
<tr>
<td>360</td>
<td>0.0299</td>
<td>0.085</td>
<td>0.042</td>
</tr>
<tr>
<td>720</td>
<td>0.0495</td>
<td>0.17</td>
<td>0.078</td>
</tr>
<tr>
<td>1440</td>
<td>0.061</td>
<td>0.21</td>
<td>0.10</td>
</tr>
</tbody>
</table>

### C. Analytical model: Second version

The strong deviation between the analytical model and the TRIDYN simulations can find its origin in several effects. Indeed, we realize that the analytical model neglects several effects, which are included in the TRIDYN code, i.e., knock-on implantation, range shortening, ion mixing, and others. However, these effects cannot, in our opinion, explain this strong deviation completely. Indeed, the major difference between the analytical model and the TRIDYN code is the approach of the chemical modification of the target. On the other hand, in the TRIDYN code the chemical reaction...
between O and Al is actually not simulated. In this way, every incoming O atom results in a decrease of the sputter yield by affecting the surface binding energy matrix. On the other hand, in the analytical model, we assume that the reaction probability of the incoming O atoms is affected by the degree of reaction $\theta$ [see Eq. (7)], i.e., the higher the degree of reaction, the more O atoms are needed for a further poisoning of the target. In this way, the critical mole fraction is shifted towards larger values. To compare both models, we can modify the analytical model in the following way. When an implanted $R$ atom encounters a matrix element $N_{ij}=1$, we can choose a new random row $i$ and repeat the implantation process, instead of assuming this atom is lost for the chemical modification of the target as in the first approach [Eq. (7)]. We can repeat this until the $R$ atom encounters a matrix element $N_{ij}=0$. Taking this approach into account, Eq. (9) becomes

$$
\frac{z' [ \gamma_{M} + \theta_{b} (\gamma_{c} - \gamma_{M}) ] \theta_{b}}{1 + z \theta_{b}} = f. 
$$

(10)

In the latter equation we have introduced two values for $z$, i.e., $z$ and $z'$. Indeed, the difference in approach between the TRIDYN code and the analytical model also has an influence on the value of $z$, the number of reactive atoms needed to form one compound molecule $MR$. In the analytical model we have set $z'=1.5$ because 1.5 O atoms are needed to form one molecule of the compound, which has a different sputter yield compared to the target material. In the TRIDYN code, each implanted O atom influences the sputter yield by affecting the surface binding energy matrix, irrespective of the number of compound molecules formed. Therefore, to compare the result of the analytical model with the TRIDYN code we must set $z'=1$. However, the value of $z$ in the denominator in Eq. (10), which accounts for the increase of atoms in the target (or density increase), remains equal to 1.5 as the maximum number of implanted O in TRIDYN is set equal to the number of O atoms in Al$_2$O$_3$. As shown in Table I, the critical mole fraction calculated using Eq. (10), approaches the TRIDYN values much better, especially for the low energy simulations. The erosion rate calculated from this analytical model, is compared in Fig. 4 with the result from TRIDYN at 360 eV.

Equation (10) predicts two interesting points, which are also reflected by the TRIDYN simulations. First, as the $\theta_{b}$ vs $f$ curve is S shaped, Eq. (10) predicts [see also Figs. 3(a) and 4] hysteresis, i.e., when starting from a poisoned target, a lower reactive gas mole fraction must be used to return to the metallic state as compared to the reverse process.

Second, we can rewrite Eq. (10) as

$$
\frac{z' \gamma_{M} ([1/r - 1] \theta_{b} + 1) \theta_{b}}{1 + z \theta_{b}} = f, 
$$

(10')

with $r$ the ratio between the sputter yield of the target material and the compound, i.e., $r = \gamma_{M}/\gamma_{c}$. From the TRIDYN results, we learn that the ratio $r$ is in the order of 10–30 depending on the ion energy. Under such conditions, Eq. (10') predicts that the critical mole fraction should vary almost linearly with the sputter yield of the metal. Using the TRIDYN model we can easily test these two predictions.

Figure 5 shows the linear relationship between the critical mole fraction $f_{cr}$ and the sputter yield $\gamma_{M}$ as calculated from the TRIDYN results. This behavior of the critical mole fraction as a function of the sputter yield of the target material can be easily understood from the analytical model. The number of implanted ions per removed monolayer is inversely proportional to the sputter yield, i.e., $2 f A / \gamma_{b}$. Therefore, as the sputter yield of the target material increases, the critical mole fraction $f_{cr}$ must increase proportionally to reach the same target condition.

In order to verify the hysteresis effect using the TRIDYN code, we have performed the simulation in the following way. After the calculation for $f=0.0$ (pure Ar bombardment) we used the output file describing the target condition as input file for the next calculation at $f=0.005$. This calculation was continued until $f=0.045$. Then using the same step $\Delta f=0.005$, we continued the calculation but now reducing the mole fraction until $f=0.0$. The result is shown in Fig. 6. As predicted from the analytical model, we notice the presence of hysteresis. Again this effect can be easily explained.

![Fig. 4. Comparison between the erosion rates of an aluminum target calculated from the analytical model (dashed line) and the TRIDYN result at 360 eV (solid line). The erosion rate was calculated using Eq. (5), and the mole fraction using Eq. (10). We used the sputter yields and density for metal and compound as given by TRIDYN.](Image 336x91 to 540x245)

![Fig. 5. Linear relation between the sputter yield of Al (calculated from the erosion rate at $f=0$ using TRIDYN) and the critical mole fraction as shown in Fig. 1 (TRIDYN results). The dotted line is a linear fit.](Image 348x612 to 528x743)

---

Starting from a metal target, we reduce the sputter yield by increasing the mole fraction of reactive gas in the plasma. At a given critical mole fraction the target becomes completely poisoned. At that point, the sputter yield equals $g_c$, which is much lower than the sputter yield of the original target material and to remove one monolayer we must also implant a large number of reactive ions. In this way, the poisoned state can be maintained at lower mole fractions compared to the reverse process of reactive gas addition. From these results it follows that the hysteresis region is very narrow [see Fig. 3(a)] in agreement with our results presented in Ref. 3.

IV. CONCLUSION

In the TRIDYN simulation and in the analytical model, we use a known mole fraction of reactive gas. Therefore, we neglect the consumption of reactive gas by the sputtered target material, i.e., the gettering process. As shown by Berg et al., the gettering process can, under certain experimental conditions, result in an abrupt change of the target condition and also hysteresis will be noticed. The simulations presented here, clearly show that an abrupt change of the target condition can also be induced by reactive ion implantation. Depending on the experimental conditions, this latter effect can be masked by the gettering process. Especially, at low pumping speed and high target current, the behavior of the target condition will be mainly dominated by the gettering process. However, under condition of high pumping speed and low target current, the ion implantation effects will be more pronounced, which is also true when the sticking coefficient of the reactive gas species on the target surface and deposited target material are low.

ACKNOWLEDGMENTS

Z. Y. Chen is financed by the Bilateral Scientific and Technological Cooperation (Joint Project No. BIL 99/46) of the Ministry of the Flemish Community, the Ministry of Science and Technology of China, and the National Science Foundation of China. A.B. is indebted to the Flemish Fund for Scientific Research (FWO) for financial support. The authors also acknowledge financial support from the Belgian Federal Services for Scientific, Technical and Cultural Affairs (DWTC/SSTC) of the Prime Minister’s Office through IUAP-V. Finally, we would like to thank W. Möller for supplying the simulation code TRIDYN (Version 4.0).