Reactive magnetron sputter deposition: a journey from target to substrate

D. Depla

Dedicated Research on Advanced Films and Targets
Ghent University

Setting the scene
- Who?
- Some keywords
- Main features of the model
Who?

Further development of the RSD model
Simulations
Koen Strijckmans
Oxide formation on the target
Roeland Schelfhout

RSD2018

December 6th and 7th.
Short course: December 5th

www.rsd2018.be
A few keywords

- Analytical approach
- Click on/off approach
- GUI to assist the user
- Main focus on the "hysteresis"

The RSD model aims to get a better insight in the reactive sputtering process. Key features are:

- Analytical approach
- Click on/off approach
- GUI to assist the user
- Main focus on the “hysteresis”

Target processes

The transport is defined by sputtering and redeposition. As we know ions get implanted, we describe the ion implantation in the bulk. Initially the implanted atoms are not chemically bonded. We describe explicitly the chemical reaction $kn_m$.

Surface processes are described as a balance between removal and addition.
Target poisoning occurs not only at the surface, but also in the submonolayers. The major contribution is reactive ion implantation. The RSD model accounts for the chemical reaction between the implanted species and the target material.

Question 1: Can we predict the first critical point?
An experiment

Target material: aluminium
Circular planar target (2 inch diameter)
Pumping speed: 35 l/s

Before the first critical point hardly an increase of the oxygen pressure

The first critical point linearly depends on the discharge current

Origin: the target and the deposited material react with the introduced oxygen.
Getter pump action.

A few experiments more...

Different conditions show a similar behaviour

Can we describe this more quantitative?
Some equations, sorry!

We assume the target is much smaller than the deposition area, or stated differently before the first critical point the gas is only consumed by the deposited material

\[ Q_{\text{getter}} = \sum \alpha_s (1 - \theta_s) A_{s,i} \]

The condition of the deposited material is given by the following balance equation

\[ \frac{2 \alpha_s}{z} F (1 - \theta_s) + \alpha_s \sigma_T (1 - \theta_s) = F_{m,s,i} \theta_s\]

But the target is hardly poisoned:

\[ Q_{\text{getter}} = \frac{\sum \epsilon_s \alpha_s \sigma_T}{2} \]

The maximum getter is just given by the product of the discharge current, and the metal sputter yield. Or the first critical point scales linearly with the current.

And what about your experiments?

Database

Your data is stored in a database (currently 120 entries, 32 different target-gas combinations)

Slope between experimental flow at the 1st critical point, and maximum getter rate is 0.541.

Engineering approach

\[ Q_{1st} \approx 3.75 \ \text{[scm]} \cdot 2 Y_{\text{metal}} \]
How good is our model?

Perform simulations (53248 in total)

Most common value for $\theta_m \theta_s : 0.575$

Simulations for different substrate areas, sticking coefficients, sputter yields, pumping speed (colour code refers to combinations)

But we also deviations from the fit ...

Deviations

Let us return to assumptions ...

Low reactive gas pressure before critical point
Not true for low reactivity materials
Only consumption by the deposited material
Not true at high pumping speeds
Only consumption by the deposited material
Not true at low discharge currents
Question 1: Can we predict the first critical point?

Answer 1: Yes, reasonably well...

![Graph showing flow at 1st critical point vs. discharge current for different argon pressures.]

Question 2: Can we predict the discharge voltage behaviour?

![Graph showing percentage of different elements vs. noble gas concentration.]

Copyright D. Depla
Experimental observation

\[
\begin{align*}
\text{M} &= \text{metal} \\
\text{X} &= \text{nitrogen/oxygen}
\end{align*}
\]

at the surface

\[
\begin{align*}
\text{M} &= \text{metal} \\
\text{X} &= \text{nitrogen/oxygen}
\end{align*}
\]

in the bulk

---

Why do we have this relation?

For high values of $R (>1)$, we have a reduced oxide (nitride) target surface. Reduced oxides (and most nitrides) are (semi)-conductors with a low electron yield or high discharge voltage during poisoning. The opposite holds for low values of $R (<1)$.

Another interpretation of $R$: it is a measure for the difficulty to form a fully stoichiometric compound during ion bombardment.

But, despite the impressive amount of experimental data supporting this idea, we need first to proof that during reactive sputtering, we indeed have a reduced oxide surface.
XPS to confirm ... reactive sputtering of Ta

A new design of a 1” magnetron always to remove the target in vacuo and transfer it to the XPS analysis chamber.

For Ta, suboxides are formed, but at high fractions, the stoichiometric oxide is observed.

XPS to confirm it ... reactive sputtering of Al

For Aluminium only the oxide and the metal are detected. No suboxides are observed.
Relation discharge voltage-oxide fraction

The discharge voltage can be correlated with the presence of the stoichiometric oxide.

The oxygen fraction during reactive sputtering, even in poisoned mode, is seldom larger than 0.2.

Question 2: can we predict the discharge voltage behaviour?

Answer 2: Yes, and we understand the mechanism.
Question 3: Do we have data on the oxide sputter yield?

Is data on the sputter yield important...?

The ratio between the metal sputter yield \(Y_m\) and the compound sputter yield \(Y_{\text{tot}}\) defines to a large extend the hysteresis phenomenon.

So, a simple conclusion is that hysteresis is caused by the lower sputter yield of compounds.

"...the authors come to the conclusion that the sputtering yield of oxides are in most cases similar to or even higher than those of the corresponding metals", and further in the same overview "For comparison, measured data for Si and Ta are included. For SiO\(_2\), the sputter yields are about the same magnitude or slightly lower than Si, but for Ta\(_2\)O\(_5\) generally higher yields than for Ta are observed"

This is the data we have...

But there is a problem...

\[ \frac{F_P}{F_m} = \frac{(x+y)D_P \rho_c}{MM_c} \]

Deposition profiles will be similar.

\[ \frac{F_P}{F_m} = \frac{\epsilon_P P_{ion} Y_{tot}}{\epsilon_m P_m} \]

Voltage are different.

\[ \frac{Y_{tot}}{Y_m} = \frac{P_{ion} F_P Y_{m,cac}}{P_m F_m Y_{m,cac}} \]  

Why is there a huge drop in deposition rate? Most points are addressed.

Bombardment by \( O_2^+ \) instead of \( Ar^+ \)?

Not always a valid argument

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (Ar)</td>
<td>0.876</td>
<td>0.688</td>
</tr>
<tr>
<td>Yield (O_2^+)</td>
<td>0.384</td>
<td>0.502</td>
</tr>
</tbody>
</table>
Can we trust the sputter yields?

Measuring the mass difference and discharge current at constant discharge voltage

Difficulties
1. Electron yield
2. Neutrals
3. Ion energy

Neutrals
Charge exchange mechanism
Window based on literature

Consistent with advanced simulations

But for oxides...

The weight loss, and so the sputter yield, as a function of the discharge current during reactive sputtering (poisoned mode) of an aluminium target.

Can we proof it in another way?

Re-deposition on the target was excluded by shielding the re-deposition areas.
An alternative way to measure the sputter yield

Balance equation

\[ q_{in} = q_p + q_s + q_t \]

\[ q_{cons} = q_s + q_t = \frac{Z}{2} I_{ion} Y_c \]

In poisoned mode, the consumption rate is directly related with the compound sputter yield.

Measure with a mass spectrometer the oxygen pressure (simple explanation)

Comparison

This new method confirms the current dependency of the sputter yield

Reason: we now work on the hypothesis that the target contains non-reacted implanted oxygen atoms. At low discharge current these atoms can diffuse from the target. At high discharge current their presence reduces the sputter yield.
Overview sputter yields

Several observations

- Not related to the target condition (see sputter cleaning experiments)
- Large difference between ratio based on ion beam experiments and deposition rate experiments

Correlation between compound sputter yields

A remarkable plot because \( R \) ensures that the flux from the target equals the compound composition. There is a big difference between ion beam (or sputter cleaning) experiments, and sputtering in poisoned mode.

The removal of an oxygen atom increases the probability to sputter a metal.

A removed oxygen atom, can be replaced by another (implanted) oxygen atom.

Outliners are probably related to texturing.
Question 3: Do we have data on the oxide sputter yield?

Answer 3: No, we have not. Moreover the mechanisms are not fully clear.

"...the authors come to the conclusion that the sputtering yield of oxides are in most cases similar to or even higher than those of the corresponding metals"; and further in the same overview "For comparison, measured data for Si and Ta are included. For SiO₂, the sputter yields are about the same magnitude or slightly lower than Si, but for Ta₂O₅, generally higher yields than for Ta are observed."


This is 35 years ago!

Question 4: And what about the time dependency of the process?
Consumption/sputter yield as a function of time (x2)

Just wait …

Discharge on

Discharge off

poison the target
switch off
the magnetron
and wait for
- 10 seconds
- 160 seconds
- 6620 seconds
- 61200 seconds

Sputtering Yield (A0, g/ton)

Sputtering time (s)

Again … can we trust this sputter yield behaviour?

Sputter cleaning to proof

Sputter cleaning experiments give information about initial target behavior

Measure cleaning time

Calculate $Y$: $t_{cleaning} \propto \frac{d}{Y}$

(With fixed thickness $d=2$ nm)

Confirmation of our experiments. Origin is probably due to diffusion of the non-reacted oxygen from the target.
Desorption

An abrupt change as a function of the reactive gas fraction is noticed. Slow outdiffusion of nitrogen is detected.

The reaction rate constant

The grey regions are based on a dedicated fitting of hysteresis experiments for Y and Al, published before this work and using other data. So, the reaction rate constant is an effective reaction rate constant $k_{n_1 n_m}$.
Answer 4: Diffusion (radiation enhanced, thermal, pressure driven) is the process we need to describe to quantify in detail our experiments. Moreover, for pulsed experiments, it will become a necessity.

Question 5: Does our traditional view show all details?
Our “traditional” view on reactive sputtering

In literature different ways are used to study the hysteresis phenomenon

**Flow control (Q)**
- Stepwise change of the reactive gas flow
- Working at constant current (I), voltage (V) or power
- Measuring the change in voltage, current and pressure (P)

**Pressure control (P)**
- Stepwise change of the reactive gas pressure
- Working at constant current (I), voltage (V) or power
- Measuring the change in voltage, current and pressure (P)

Of course, voltage control is also possible. It has several advantages.
It is fast, easy and permits to work in a “random” way to exclude any long term effects such as target erosion.

**PVIQ plot: metallic to poisoned mode**

- high pressure, low voltage
- Poisoned mode
- low pressure, high voltage
- Metallic mode
Comparison with common plots (projections from (P,V,I,Q))

- I-V characteristic for the poisoned mode
- I-V characteristic for the metallic mode

PVIQ plot: metallic to poisoned mode

- High pressure, low voltage
- Poisoned mode
- Low pressure, high voltage
- Metallic mode
When don’t get the same result when the (P,Q,I,V) space is accessed in a different direction.

So forward and back is different
Double hysteresis

Origin:

1. An avalanche due the gettering capacity of the deposited material which cause a single S (see first critical point).
2. An avalanche due to the reaction kinetics of the implanted reactive ions which causes the double S.

The existence of a double S-shaped process curve during reactive magnetron sputtering
R. Schelfhout, K. Strijckmans, D. Depla

Origin of the double hysteresis: a possible answer
Question 5: Does our traditional view show all details?
Answer 5: No. The new approach confirms the model, but adds new challenges.

We observe a double hysteresis in the simulations, but the fit with the experiment is not completely successful.