What can we learn from modelling of reactive magnetron sputtering?

D. Depla, K. Strijckmans

Design, Research And Feasibility of Thin Films
Ghent University

The processes

- Sputtering
- Chemisorption
- Knock on and direct implantation
- (Re)deposition
Sputtering (1)

A strong need for sputter yields not only for oxides but also for metals.

Quantification of target erosion/deposition rate

Measuring the mass difference and discharge current at constant discharge voltage

\[ Y = \frac{\Delta m}{nM} = \frac{I}{1 + \gamma_{\text{ISEE}}} \]

Difficulties
1. Electron yield
2. Neutrals
3. Ion energy (see \( f_{\text{ion}} \))

On the effective sputter yield during magnetron sputter deposition
D. Depla NIMB 328 (2014) 65

Sputtering (2)

For oxides: data has been obtained for \( Y_2O_3 \) and \( Al_2O_3 \)
See later...

Neutrals
Charge exchange mechanism
Window based on literature

Consistent with advanced simulations

Consistent with advanced simulations

M.J. Goeckner, J.A. Goree, T.E. Sheridan
Chemisorption: target (1)

After exposing the target to oxygen the target is sputter cleaned.

The sputter cleaning time allows to calculate the thickness.

Chemisorption: target (2)

Good agreement with literature on the oxidation rate

So, no influence of the bombardment prior to the oxygen exposure

But the plasma does not contain only O₂. See later...

This story however shows another important message.

Chemisorption: target (3)

How clean is a target during sputtering?

![Image](image_url)

Chemisorption: substrate (1)

Method:

\[
\text{In corporation coefficient} = \frac{\text{Amount in the layer}}{\text{Amount arriving}}
\]

- # depositions at same conditions
- oxygen flow
- argon pressure
- pumping speed
- discharge current
- T-S distance
- chamber geometry
- # depositions WITH fixed, small oxygen flow
- # depositions WITHOUT fixed oxygen flow to account for the background gases

EPMA

\[
\phi_{\text{in layer}} = \phi_{\text{ox,layer}} - \phi_{\text{ox,background}}
\]

Mass Spectrometry at the position of the substrate under the same conditions as the depositions

![Image](image_url)
The processes

The model

The parameters

The examples

Conclusions

Chemisorption: substrate (2)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>T-S distance</th>
<th>Ar pressure</th>
<th>(O_2/Ar)</th>
<th>(I_{\text{discharge}})</th>
<th>(P_{\text{en}})</th>
<th>(\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>15 cm</td>
<td>0.34 Pa</td>
<td>2.9/20</td>
<td>0.47 A</td>
<td>2.53 x 10^{-4} Pa ± 0.67 x 10^{-4} Pa</td>
<td>0.170 ± 0.032</td>
</tr>
<tr>
<td>Yttrium</td>
<td>8 cm</td>
<td>0.34 Pa</td>
<td>1.5/20</td>
<td>0.47 A</td>
<td>5.54 x 10^{-5} Pa ± 1.15 x 10^{-5} Pa</td>
<td>0.230 ± 0.043</td>
</tr>
<tr>
<td>Magnesium</td>
<td>10 cm</td>
<td>0.34 Pa</td>
<td>2.5/20</td>
<td>0.47 A</td>
<td>2.53 x 10^{-4} Pa ± 0.67 x 10^{-4} Pa</td>
<td>0.170 ± 0.032</td>
</tr>
<tr>
<td>Copper</td>
<td>15 cm</td>
<td>0.34 Pa</td>
<td>1.5/20</td>
<td>0.47 A</td>
<td>1.57 x 10^{-2} Pa ± 0.75 x 10^{-2} Pa</td>
<td>0.0046 ± 0.0003</td>
</tr>
</tbody>
</table>

Knock-on and direct implantation

A similar scheme as for chemisorption on the target, but now the target is oxidized by exposure to an oxygen plasma.

This time scale is only understandable when oxygen is implanted.
Knock on and direct implantation

We assume that all nitrogen is bonded to titanium.

But thicknesses fit nicely with implantation range of nitrogen ions into titanium at energies defined by the discharge voltage.

(Re)deposition

SIMTRA is particle trajectory code.

New version with improved GUI is available … for free.

Building the vacuum chamber
The fraction of sputtered material returning to the target scales almost linearly with the argon pressure.

Target redeposition is high in the racetrack but this is not important as it is balanced by the erosion process. However, outside the racetrack oxide formation will occur.
**Target description**

- 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 $k_{r,n} n_m$.

**Surface processes** are described as a balance between removal and addition.

**Target surface description**

- Derivation based on conservation of particles $M$ and $MR_z$.
- One example:

\[
\begin{align*}
\text{Transport: } & \ j_Y M \theta_M (1 - \theta_b) + j_Y F \theta_F (1 - \theta_b) + j_Y C \theta_C (1 - \theta_b) \\
\text{Chemisorption: } & \ \theta_M (1 - \theta_b) + \theta_F (1 - \theta_b) + \theta_C (1 - \theta_b) \\
\text{Sputtering: } & \ j_Y M \theta_M \\
\text{Redeposition: } & \ (F_m + F_c) \theta_c \\
\end{align*}
\]
**Substrate condition**

Similar story for the substrate

RSD2013=
critical revision of RSD2009
- Two discrete layer + subsurface
- Saturation limit
- Redefining surface equations

Simulations are possible in steady-state and time
Multi-cell approach for both target and substrate

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**“The Chinese menu card” approach**

<table>
<thead>
<tr>
<th>Solution:</th>
<th>Steady</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform deposition</td>
<td>C,D,E</td>
<td>A,B</td>
</tr>
<tr>
<td>No redeposition</td>
<td>D,E</td>
<td>A,B,C</td>
</tr>
<tr>
<td>Uniform current</td>
<td>B,C,D,E</td>
<td>A</td>
</tr>
<tr>
<td>No saturation limit</td>
<td>E</td>
<td>A,B,C,D</td>
</tr>
</tbody>
</table>

Deposition profile
- C,D,E
- A,B

Redeposition
- D,E
- A,B,C

Non-uniform current
- B,C,D,E
- A

Oxygen pressure $P_{O_2}$ (mbar) vs. Oxygen flow $Q_{O_2}$ (sccm)

RSD2013 simulation
- A
- B
- C
- D
- E

Saturation limit
- E
- A,B,C,D
The processes

The model

The parameters

The examples

Conclusions

Running RSD2013

Command line

Graphical user interface (GUI)

Manual

Free download

K. Strijckmans and D. Depla

The parameters

What do we know?

What we don’t know!

Fitting experiments

What can we learn?

I’m inventing a robot to make the RGB, but I need a grant. Can I have one?
Input parameters: the quest

Problem: 2 unknown parameters ($\alpha$, $k$)
Reason: experimentally or by simulation hard to retrieve (even for Y₁)
Goal: fit freedom and material dependency
Solution: fitting RSD model to experiments

Experimental setup

Sputter conditions:
- Target Al or Y (D = 2")
- Process gas Ar
- Reactive gas O₂
- $S$ = 55 L/s or 112 L/s
- $P_{base}$ = ~10⁻⁴ Pa
- $P_{Ar}$ = 0.45 Pa or 0.37 Pa
- $I$ = 0.4 A, 0.5 A or 0.6 A

Hysteresis experiment = stepwise in/decreasing the O₂ flow while collecting

steady state values V, I and $P_{tot}$
Fitting procedure

Fit criteria = 6 critical O₂ flow values
• goodness of the fit = worst match out of 6
• fits are ‘good’ if critical points fall within acceptance tolerance \( f_a \)

Simulation includes
- measured \( V \) and \( I \) variation \( Y_m \) and \( I_{\text{ion}} \)
- changing target oxidation oxygen implantation profile \( I_{\text{ion}} \) (by \( Y_{\text{SEE}} \))

Scan algorithm

Serial implementation illustrated for a 2-D parameter space \((X,Y)\)

Goal: finding all \((x_i,y_i)\) combinations that pass the fit criteria

Ingredients:
- starting point (Start) \( \Rightarrow \) found by (slightly) modified version
- step size \( (\Delta x, \Delta y) \)
- parameter boundaries
- fit procedure + acceptance tolerance \( f_a (>1) \)
- three lists: rejected, accepted and unfinished

Limitation: only for a connected region
Fitting results: correlations

- one-cell target ($f_a = 1.5$) vs. experimental $Y_c$
- multi-cell target ($f_a = 3$) vs. experimental $Y_c$

Fitting results: analysis

- Reaction coefficient $k$ and sputter yield oxide $Y_c$ highly correlated
- Power law $Y_c = b' k^a$
- Ratio $Y_{Al}/Y_c$ and correlation independent of:
  - reaction coefficient $k$
  - one-cell or multi-cell target
  - implantation profile
Fitting: some remarks (1)

Using the experimental oxide sputter yields, we get a quite similar reaction rate for Y and Al with implanted O atoms.

Restricting the possible reaction rate constants to the same values and within the range of the experimental oxide sputter yields, we get a value for the sticking coefficient on the target.

\[
\begin{align*}
\text{Al} & : 0.08 \pm 0.046 \\
\text{Y} & : 0.53 \pm 0.14
\end{align*}
\]

How this compares to literature?

- Aluminium: 0.0136 (average value over 6 different papers)
- Yttrium: 0.44 (combination of 2 papers)

The fitted values are much higher: ion stimulated chemisorption, but mainly the presence of atomic oxygen (sticking coefficient 1).

Fitting: some remarks (2)

Atomic flux to the molecular flux is order 0.1

\[
\alpha_{\text{Al}} = \frac{0.1 + 0.0136}{1 + 0.1} = 0.10 \\
\alpha_{\text{Y}} = \frac{0.1 + 0.44}{1 + 0.1} = 0.49
\]

So, not only the sputter yields fit, but also the sticking coefficients.

\[
\begin{align*}
\text{Al} & : 0.08 \pm 0.046 \\
\text{Y} & : 0.53 \pm 0.14
\end{align*}
\]
The examples

- Discharge voltage behaviour
- Target rotation
- Target erosion
- Argon pressure influence

Discharge voltage behaviour

Flow

Duty cycle between 100% and 0%

Target: Al (406.4x127 mm)
Reactive gas: O₂
Constant current: 2 A
Argon flow: 50 sccm

Measurement performed at ENSAM (Cluny, France)
With cooperation of A. Besnard, N. Martin
Details

Discharge voltage for a poisoned target in Ar/O₂
Small decrease when oxygen is removed
Simple: effective ionisation energy of Ar is lower as compared to oxygen

Discharge voltage for a metal target in pure argon
Small increase on reactive gas addition...
Why?

We see this slight increase when the oxygen pressure change is small.

Simulation: the coverage by chemisorption results in a voltage increase, while compound formation results in voltage decrease.
Hysteresis shifts to lower oxygen flow on increasing the rotation speed

Target rotation (1)

Target rotation (2)
Target rotation: sputter cleaning

Sputtering a stationary target, and then sputter cleaning in pure argon while rotating.

X.Y. Li, D. Depla, W.P. Leroy, J. Haemers, R. De Gryse
In poisoned mode: faster sputter cleaning than in metallic mode
Reason: the deposited layer is much thinner because the deposition rate is much lower

Target rotation: simulations
Including deposition enables to mimic the sputter cleaning experiments
• $\Delta S$ enters plasma region fully oxidized
• increase RPM $\rightarrow$ smaller $t_o$ = less time for oxide removal
• critical gas flow decreases with increasing RPM

Without deposition, we would expect a similar behaviour, i.e., 1/RPM behaviour

Lower rotation speed means a thicker layer, but there is more time to sputter the layer
Higher rotation speed means a thinner layer, but there is less time to sputter the layer
Target erosion

Shifting of both critical points to lower oxygen flows.

- **1st critical point:**
  the redeposition acts as a sink for sputtered metal
  it reduces the metal flux towards substrate, which more easily gets oxidized

- **2nd critical point:**
  the redeposition of sputtered compound material keeps the target oxidized

The effect on the “racetrack”

Prolonged sputtering in poisoned mode results in a different racetrack as compared to metallic mode.
Sputter profile

racetrack profile ≠ sputter profile

Influence of the pressure...
The processes are relatively well understood and described.

The model is (too) simple but gives quantitative results, ...

But the parameters are hard to get, and needs dedicated experiments.

N. Mason in “The plasma 2012 roadmap”
“Developing such models and gaining a detailed understanding of the physical and chemical mechanisms within plasma systems is intricately linked to our knowledge of the key interactions within the plasma and thus the status of the database for characterizing electron, ion and photon interactions with those atomic and molecular species within the plasma and knowledge of both the cross-sections and reaction rates for such collisions, both in the gaseous phase and on the surfaces of the plasma reactor.”
## Acknowledgements

<table>
<thead>
<tr>
<th>Further development of the RSD model</th>
<th>Simulations</th>
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<tbody>
<tr>
<td>Koen Strijckmans</td>
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<tr>
<td>Measurements of incorporation coefficients and sputter yields</td>
<td></td>
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<tr>
<td>Wouter Leroy</td>
<td></td>
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<tr>
<td>Further developments of the SiMTRA code</td>
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<tr>
<td>Francis Boydens</td>
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<tr>
<td>Oxide formation on the target</td>
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<td>Roeland Schelfhout</td>
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