A modelling view on the existence of hysteresis during reactive HiPIMS

K. Strijckmans, D. Depla

Dedicated Research on Advanced Films, and Targets
Outline

1. Introduction
2. RSD models
3. Simulation study
4. RSD+IR model
5. Conclusion
Reactive HiPIMS: hysteresis?


Reactive HiPIMS: hysteresis?

Hysteresis?  
- 9 yes  
- 21 no  
- 8 undecided

38 hystereses out of 18 papers  
- limited data  
- undecided = fast ramping  
- no conclusions
<table>
<thead>
<tr>
<th>Introduction</th>
<th>RSD models</th>
<th>Simulation study</th>
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<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Introduction</td>
<td>2 RSD models</td>
<td>3 Simulation study</td>
<td>4 RSD+IR model</td>
<td>5 Conclusion</td>
</tr>
</tbody>
</table>
## Variables in RSD model

<table>
<thead>
<tr>
<th>System part</th>
<th>Resolved variable</th>
<th>Model approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chamber</td>
<td>$P$, $Q_p$</td>
<td>one-cell</td>
</tr>
<tr>
<td></td>
<td>reactive partial pressure, gas flow to pump</td>
<td></td>
</tr>
<tr>
<td>Target</td>
<td>$Q_t$, $\theta_m$, $\theta_c$, $\theta_r$, $n_m(x)$, $n_r(x)$</td>
<td>one-cell, uniform current, multi-cell, non-uniform current, depth profile, SRIM implantation</td>
</tr>
<tr>
<td>• Surface</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Subsurface</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Substrate</td>
<td>$\theta_s$, $Q_s$</td>
<td>one-cell, multi-cell, SIMTRA profile</td>
</tr>
<tr>
<td></td>
<td>chemisorbed fraction, gas flow consumption</td>
<td></td>
</tr>
</tbody>
</table>

### 5 BALANCE equations ↔ 5 ODE's

\[ 0 = f(y) \leftrightarrow \frac{dy}{dt} = f(y) \]

### Steady state ↔ Time

\[ 0 = f(y, \frac{\partial y}{\partial x}) \leftrightarrow \frac{\partial y}{\partial t} = f(y, \frac{\partial y}{\partial x}) \]
Processes in RSD2013

**Target**

sputtering

- Metal M
- Chemisorbed MR
- Reacted MR
- Reactive molecule R₂
- Inert gas Ar
- Reactive atom R
Processes in RSD2013

Target

sputtering

direct implantation

- metal M
- chemisorbed MR
- reacted MR
- reactive molecule $R_2$
- inert gas Ar
- reactive atom $R$
Processes in RSD2013

Target

- sputtering
- direct implantation
- knock-on implantation

Legend:
- metal M
- chemisorbed MR
- reacted MR
- reactive molecule $R_2$
- inert gas Ar
- reactive atom R
Processes in RSD2013

Target

- sputtering
- direct implantation
- knock-on implantation

Reaction

- metal M
- chemisorbed MR
- reacted MR
- reactive molecule R₂
- inert gas Ar
- reactive atom R
Processes in RSD2013

Target
- sputtering
- direct implantation
- knock-on implantation

Target & substrate
- deposition

Reaction:
- metal M
- chemisorbed MR
- reacted MR
- reactive molecule R₂
- inert gas Ar
- reactive atom R

Introduction RSD models Simulation study RSD+IR model Conclusion
Processes in RSD2013

Target
- sputtering
- direct implantation
- knock-on implantation

Target & substrate
- deposition
- chemisorption

reaction
- metal M
- chemisorbed MR
- reacted MR
- reactive molecule R₂
- inert gas Ar
- reactive atom R

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RSD models
Simulation study
RSD+IR model
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### Running RSD2013 software

#### Command line

- ![Command line screenshot](image1.png)

#### Graphical user interface (GUI)

- ![GUI screenshot](image2.png)

#### Manual

- ![Manual screenshot](image3.png)

#### Free download

- **SRIM**
  - [www.srim.org](http://www.srim.org)
- **SIMTRA v2.2.1-beta**
  - [www.DRAFT.ugent.be](http://www.DRAFT.ugent.be)
- **RSD2013 v1**
  - [www.DRAFT.ugent.be](http://www.DRAFT.ugent.be)
Model modifications ...

- **RSD**
  - Current pulses
    - Inherent time dependent (only time solution)

- **RSD**
  - Different oxygen ‘activation’
    - Sticking coefficient lowers during pulse off-time

- **RSD**
  - Metal ionization and implantation
    - Combined ionization-return probability $\varepsilon_{M^+}$ for sputtered metal atom
    - Metal implantation profile
    - Density relaxation is included

**Study the effect on the hysteresis of ...**

- Enhanced target cleaning?
- Lower surface reactivity by pulse off-time (and gas rarefaction)
- High dose of metal implantation
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Reference system

Start from a reference DC system of Al in Ar/O₂

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>RSD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Y_m )</td>
<td>0.756</td>
<td>sputter yield of metal atoms M</td>
</tr>
<tr>
<td>( Y_n, Y_c )</td>
<td>0.06</td>
<td>sputter yield of compound molecules MR(_n), chemisorbed molecules MR(_c)</td>
</tr>
<tr>
<td>( \alpha_t )</td>
<td>0.1</td>
<td>sticking probability of reactive gas on metal for target</td>
</tr>
<tr>
<td>( \alpha_s )</td>
<td>0.1</td>
<td>sticking probability of reactive gas on metal for substrate</td>
</tr>
<tr>
<td>( k ) [cm(^3) s(^{-1}) #M(R(_z)) (^{-1})]</td>
<td>5·10(^{-23})</td>
<td>reaction rate coefficient of implanted reactive atoms with metal particles</td>
</tr>
<tr>
<td>( \beta ) [#R ion(^{-1})]</td>
<td>0.2</td>
<td>knock-on yield of chemisorbed reactive atoms</td>
</tr>
<tr>
<td>( p(x) ) [cm(^{-1})]</td>
<td>( R_p=1.4 \text{ nm} ) ( dR_p=0.8 \text{ nm} )</td>
<td>mean of Gaussian implantation profile of reactive atoms deviation of Gaussian implantation profile of reactive atoms</td>
</tr>
<tr>
<td>( n_0 ) [#M(R(_z)) cm(^{-3})]</td>
<td>6.03·10(^{22})</td>
<td>particle density</td>
</tr>
<tr>
<td>( z )</td>
<td>1.5</td>
<td>stoichiometric factor</td>
</tr>
<tr>
<td>( I ) [A]</td>
<td>0.286</td>
<td>discharge current</td>
</tr>
<tr>
<td>( P_i ) [Pa]</td>
<td>0.4</td>
<td>inert working gas pressure</td>
</tr>
<tr>
<td>( T ) [K]</td>
<td>300</td>
<td>gas temperature</td>
</tr>
<tr>
<td>( V ) [cm(^3)]</td>
<td>12500</td>
<td>volume of vacuum chamber</td>
</tr>
<tr>
<td>( A_t ) [cm(^2)]</td>
<td>10</td>
<td>area of target</td>
</tr>
<tr>
<td>( A_s ) [cm(^2)]</td>
<td>1000</td>
<td>area of substrate</td>
</tr>
<tr>
<td>( S ) [L s(^{-1})]</td>
<td>48.54</td>
<td>gas pumping speed</td>
</tr>
</tbody>
</table>

Low sticking probability

- Constant current mode
- Average power
  - metallic mode ~100 W
  - poisoned mode ~70 W

Relative low working pressure

Keep it simple:
- one-cell target
- one-cell substrate

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RSD2016, Ghent

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Operation pressure Argon

What’s the influence of the working pressure in DC?
- depends on surface reactivity of gas on target material
- hysteresis vanishes for low surface reactivity (like Al and Ti) at higher working pressure

⇒ HiPIMS “often” at higher working pressure

\[
\alpha_t = 0.1
\]

\[
\alpha_t = 1
\]
Current pulses

What’s the influence of the current pulses?

- characterized by frequency \( f \), duty cycle \( d \) and pulse \( p \) (=d/f)
- typical HiPIMS frequencies (100 Hz-10 kHz) and duty cycle (1-10 %)
- only effect at order 1 Hz

⇒ reactive time dynamics are slower (~1s)

Equivalent for 10 Hz, 100 Hz, 10 kHz

constant average power 100 W
Target cleaning

Time dynamics of target poisoning and sputter cleaning for DC and for HiPIMS (f=1kHz)

What’s the influence of the average power?

- Similar as for the DC regime
  - cleaning time scales inversely with power
  - poisoning time is only at higher power prolonged
- Way of power delivery only starts to matter at high power
- Depoisoning target retarded compared to reactive pressure
Gas reactivity

What’s the influence of the gas reactivity?

❖ Sticking coefficient target & substrate: 0.1 during pulse-on time
   0.01 during pulse-off time

❖ Chemisorption is suppressed compared to subsurface oxidation

❖ Gas rarefaction would give similar behavior
Returning metal

What’s the influence of returning metal in DC?

redeposition on the surface of neutral metal eliminates the hysteresis as the 1\textsuperscript{st} critical point shifts faster than the 2\textsuperscript{nd} but for HiPIMS it are metal ions

metal enrichment in subsurface equivalent with lower oxide production or reaction rate $k$
Metal implantation

What’s the influence of the metal implantation?

- combined effect of “redeposition” and “reaction rate”
- similar effect for DC and HiPIMS case
- hysteresis shifts to lower oxygen flows and narrows with increasing fraction of metal ions

⇒ reduction of hysteresis (but slower than only redeposition)
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IRM for HiPIMS plasma

IRM
= Ionization Region Model
= global (volume-averaged) model for HiPIMS plasma

... since 2008 by Gudmundsson et al.
and intensively expanded

This work “simple version” (Raadu, et al.)
ONE “true” fit parameter $F_{pwr}$

Global model for reactive HiPIMS deposition = integrate IRM into modified RSD2013

Four system parts:
1. chamber (0 D)
2. substrate (2 D)
3. target (1D)
4. ionization region (0 D)
RSD + IRM = RSD+IR

RSD variables remain but flow $q_t$ into target becomes flow $q_t$ into IR
IR species

- Neutrals: $\text{Ar, } \text{Ar}^+_m, \text{O}_2, \text{O}$
- Sputtered: $\text{Al, } \text{O}_h$ : directed flux
- Ions: single charged

Electron:

- $T_e$ power balance
- $n_e$ from quasi-neutral condition
Input for RSD+IR

Sputter conditions:
- Target Al (D = 2”)
- Process gas Ar
- Reactive gas O₂
- Pumping speed $S = 50 \text{ L/s}$
- $P_{Ar} = 0.8 \text{ Pa}$
- Frequency 500 Hz
- Pulse width 50 μs
- Duty cycle 2.5 %

Input of IVt characteristics
- metal ($\theta_m=1$) and poisoned ($\theta_m=0$) mode
- transition ($0 < \theta_m < 1$) mode

\[ I = I_m \theta_m + I_r (1-\theta_m) \quad \text{and} \quad V = V_m \theta_m + V_r (1-\theta_m) \]

\[ F_{pwr} = F_{pwr, m} \theta_m + F_{pwr, r} (1-\theta_m) \]
Locking fitting parameter $F_{pwr}$

- $\theta_m = 1$
  - $F_{pwr} = 0.4$
- $\theta_m = 0.66$
- $\theta_m = 0.27$
- $\theta_m = 0$
  - $F_{pwr} = 0.3$
First result

What does this model say?
- all previous effects are now included
- hysteresis shifts to lower oxygen flows but does not narrow (yet?)
- signature of implantation of returning metal

but ...
- we chose a too simple IRM version
- ion metal fraction is only ~20 % (HiPIMS) which is expected to double
- can we transfer our model parameters from DC to HiPIMS?

**Graph**

- f = 1 kHz
- $P_{av} = 100$ W
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Future advances

For IR model ...
- potential difference over IR
- two populations electrons “cold” and “warm”
- electron heating = sheath energization + Ohmic heating
- more species (?), more reactions (?)
- speed-up the RSD+IR calculation

For a future RSD model ...
- full atomic target description
- recoil/ion mixing
- (ion enhanced) diffusion processes

For experimentalists ...
- a systematic survey
1. Knowledge of reactive DC sputtering can guide us to the unravel the existence conditions for a hysteresis during reactive HiPIMS.

2. Extensions of the RSD model are used to study the impact of several effects claimed to eliminate the hysteresis during reactive HiPIMS.

3. A first coupling between the RSD2013 model and the IR model is established.

4. Implantation of ionized sputtered metal seems to dominate the hysteresis behavior.

5. For a definite answer, more experimental data and modelling is needed.
Acknowledgements

DRAFT colleagues:

"Target on growth"

High Performance Computing