Modeling the current waveform in reactive high power impulse magnetron sputtering

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Introduction

- Reactive sputtering, where metal targets are sputtered in a reactive gas atmosphere to deposit compound materials is of utmost importance in various technologies.

- In reactive sputtering processes a reactive gas $\text{O}_2$, $\text{N}_2$, or $\text{CH}_4$ etc. is mixed to the noble working gas for oxide, nitride, or carbide deposition.

- HiPIMS deposition generally gives denser, smoother films and higher crystallinity than dcMS grown films.

Helmersson et al. (2006) Thin Solid Films 513 1
Magnus et al. (2012) IEEE EDL 33 1045
HiPIMS - Voltage - Current - Time characteristics
In **non-reactive** discharge the current waveform shows an initial pressure dependent peak that is followed by a second phase that is power and material dependent.

The initial phase is dominated by gas ions, whereas the later phase has a strong contribution from self-sputtering.

The non-reactive case is well understood.

From Gudmundsson et al. (2012), JVSTA 30 030801
Modeling the current waveform in reactive high power impulse magnetron sputtering

**HiPIMS - Voltage - Current - time**

- Ar discharge with Ti target
- The initial peak in current results in a large flux of atoms from the target
- Collisions of the sputtered atoms with the working gas result in heating and expansion of the working gas – **rarefaction**
- A significant fraction of the sputtered atoms experience electron impact ionization (the ionization mean free path $\sim 1$ cm) and are attracted back to the target to participate in the sputtering process – **self-sputtering**

From Magnus et al. (2011) JAP 110 083306
During reactive sputtering, a reactive gas is added to the inert working gas.

The current waveform in the reactive Ar/N\textsubscript{2} HiPIMS discharge with Ti target is highly dependent on the pulse repetition frequency.

N\textsubscript{2} addition changes the plasma composition and the target condition can also change due to the formation of a compound on its surface.

After Magnus et al. (2011) JAP 110 083306
Similarly for the Ar/O$_2$ discharge, the current waveform is highly dependent on the repetition frequency and applied voltage which is linked to oxide formation on the target.

The current is found to increase significantly as the frequency is lowered.

After Magnus et al. (2012), JVSTA 30 050601
As the oxygen flow is increased a transition to oxide mode is observed.

The current waveforms for an Ar/O\textsubscript{2} discharge with a Ti target where the oxygen flow rate is varied – 600 V, 50 Hz and 0.6 Pa

From Gudmundsson et al. (2013), ISSP 2013, p. 192

Similar behaviour has been reported for various target and reactive gas combinations

- The current increases with decreased repetition frequency
- The current waveform maintains its shape for Ar/O$_2$ discharge with Nb target

From Hála et al. (2012), JPD 45 055204

- The current waveform becomes distinctly triangular for Ar/N$_2$ discharge with Hf target

From Shimizu et al. (2016), JPD 49 065202
The current increases with increased partial pressure of the reactive gas.

- The current waveform becomes distinctly triangular for Ar/N\textsubscript{2} discharge with Al target.
  
  From Moreira et al. (2015), JVSTA 33 021518

- The current waveform maintains its shape for Ar/O\textsubscript{2} discharge with Nb target.

  From Hála et al. (2012), JPD 45 055204
Modeling the current waveform in reactive high power impulse magnetron sputtering

HiPIMS - Voltage - Current - time

- At high frequencies, nitride or oxide is not able to form between pulses, and self-sputtering by Ti\(^+\)-ions (singly and multiply charged) from a Ti target is the dominant process.
- \(\gamma_{\text{sputter}}\) is practically zero for singly charged metal ions impacting a target of the same metal.
- At low frequency, the long off-time results in a nitride or oxide layer being formed on the target surface and self-sputtering by Ti\(^+\)- and N\(^+\)-ions or O\(^+\)-ions from TiN or TiO\(_2\) takes place.

Ionization region model studies of reactive HiPIMS
The ionization region model (IRM) was developed to improve the understanding of the plasma behaviour during a HiPIMS pulse and the afterglow.

The main feature of the model is that an ionization region (IR) is defined next to the race track.

The IR is defined as an annular cylinder with outer radii $r_{c2}$, inner radii $r_{c1}$ and length $L = z_2 - z_1$, extends from $z_1$ to $z_2$ axially away from the target.

From Raadu et al. (2011), PSST 20 065007
Ionization region model studies of reactive HiPIMS

The species assumed in the IRM are

- electrons
- argon atoms \(\text{Ar}(3s^23p^6)\), warm argon atoms in the ground state \(\text{Ar}^\text{W}\), hot argon atoms in the ground state \(\text{Ar}^\text{H}\), \(\text{Ar}^\text{m}(1s_5\text{ and }1s_3)(11.6\text{ eV})\), argon ions \(\text{Ar}^+\) (15.76 eV)
- titanium atoms \(\text{Ti}(a^3\text{F})\), titanium ions \(\text{Ti}^+(6.83\text{ eV})\), doubly ionized titanium ions \(\text{Ti}^{2+}(13.58\text{ eV})\)
- oxygen molecule in the ground state \(\text{O}_2(X^3\Sigma^-)\), the metastable oxygen molecules \(\text{O}_2(a^1\Delta_g)(0.98\text{ eV})\) and \(\text{O}_2(b^1\Sigma_g)(1.627\text{ eV})\), the oxygen atom in the ground state \(\text{O}(^3\text{P})\), the metastable oxygen atom \(\text{O}(^1\text{D})(1.96\text{ eV})\), the positive ions \(\text{O}_2^+(12.61\text{ eV})\) and \(\text{O}^+(13.62\text{ eV})\), and the negative ion \(\text{O}^-\)

Ionization region model studies of reactive HiPIMS

- The particle balance equation for a particular species is given by

\[ \frac{dn_{\text{species}}}{dt} = \sum R_{\text{species,process}} \]

- The reaction rate \( R_{j,\text{volume}} \) for a given volume reaction of a species \( j \) is

\[ R_{j,\text{volume}} = k \times \prod n_{r,i} \quad [\text{m}^{-3}\text{s}^{-1}] \]

- The rate at which species are sputtered off the target (Ti and O) is

\[ R_{\text{n,sputt}} = \frac{\sum_i \Gamma_i^{RT} S_{RT} Y_i(E)}{V_{IR}} \]

and \( i \) stands for the ion involved in the process, here \( i = Ti^+, Ti^{2+}, Ar^+, O^+, \) and \( O_2^+ \). \( \Gamma_i^{RT} \) is the flux of ion \( i \) towards the target.
For each ion there is a loss rate given as

$$R_{i,\text{loss}} = -\frac{\Gamma_{i}^{BP} S_{BP} + \Gamma_{i}^{RT} S_{RT}}{V_{IR}}$$

where $i$ stands for the particular ion and $S_{BP}$ is the area of the annular cylinder facing the lower density plasma outside the IR (bulk plasma), and $\Gamma_{i}^{BP}$ is the flux of ion $i$ across the boundary towards the lower density plasma.

Thus the flux out of the IR towards the lower density plasma is reduced as required to obtain the assumed ion back-attraction probability $\beta$.

$$\Gamma_{i}^{BP} = \left(\frac{1}{\beta} - 1\right) \frac{S_{IR}}{S_{BP}} \Gamma_{i}^{RT}$$
Ionization region model studies of reactive HiPIMS

- Gas rarefaction lowers the density of the process gas inside the IR below the value in the surrounding gas reservoir, \( n_{g,0} \)
- This gives a back-diffusion (gain) term

\[
R_{g,\text{refill}} = \frac{1}{2} v_{\text{ran}} \left( n_{g,0} - n_g \right) S_{RT} \frac{S_{RT}}{V_{IR}}
\]

where the subscript \( g \) stands for the atoms and molecules of the working gas \( \text{Ar} \) and \( \text{O}_2 \)
The return flux of recombined positive argon ions $\text{Ar}^+$ from the target is treated as two groups of atoms with different temperatures:

- a hot component $\text{Ar}^H$ that returns from the target with a typical sputter energy of a few electron volts
- a warm component $\text{Ar}^W$ that is assumed to be embedded in the target at the ion impact, and then return to the surface and finally leave with the target temperature, at most 0.1 eV

Thus there is a loss out of the IR

$$R_{\text{Ar}^Z, \text{loss}} = -v_{\text{ran}} n_{\text{Ar}^Z} \frac{S_{\text{RT}}}{V_{\text{IR}}}$$

where $Z$ stands for $H$ for hot or $W$ for warm argon atoms.
In addition there is a change in the neutral density due to kick-out by collisions with fast sputtered atoms coming from the target.

For each of the neutrals $Y$ of the working gas, including each of the metastable states, the particle balance includes a loss term

$$R_{n, \text{kick-out}} = -\frac{1}{2} \frac{v_{\text{ran}, X}}{L} F_{\text{coll}} \frac{m_X}{m_Y} \sum n_{X,i} \frac{\sum_i n_{Y,i}}{n_Y}$$

The sum is taken over all the states of that sputtered species and

$$F_{\text{coll}} = 1 - \exp \left( -L/\lambda_{X, \text{gas}} \right)$$

is the probability of a collision inside the IR, where $\lambda_{X, \text{gas}}$ is the mean free path for an atom $X$ sputtered off the target.
Ionization region model studies of reactive HiPIMS

- The sputter yield for the various bombarding ions was calculated by TRIDYN for
  - **Metal mode** – Ti target
  - **Poisoned mode** – TiO$_2$ target

- The yields correspond to the extreme cases of either clean Ti surface and a surface completely oxidized (TiO$_2$ surface)

- The sputter yield is much lower for poisoned target

The sputter yield data is from Tomas Kubart, Uppsala University
The model is applied to explore Ar/O$_2$ discharge with Ti target in both metal mode and oxide (poisoned) mode.

The IRM is a semi-empirical model in the sense that it uses a measured discharge current waveform as a main input parameter.

For this study we use the measured curve for Ar/O$_2$ with Ti target at 50 Hz for metal mode and at 15 Hz for poisoned mode.

After Magnus et al. (2012), JVSTA 30 050601
The gas rarefaction is observed for the argon atoms but is more significant for the O\textsubscript{2} molecule.

The density of Ti atoms is higher than the O\textsubscript{2} density.

The atomic oxygen density of is over one order of magnitude lower than the molecular oxygen density – the dissociation fraction is low.

The temporal evolution of the neutral species with 5 % oxygen partial flow rate for Ar/O\textsubscript{2} discharge with Ti target in metal mode.

Gudmundsson et al. (2016), PSST, accepted 2016
Gas rarefaction is observed for both argon atoms and \( \text{O}_2 \) molecules.

The density of Ti atoms is lower than both the \( \text{O}_2 \) density and atomic oxygen density.

The atomic oxygen density is higher than the \( \text{O}_2 \) density towards the end of the pulse.

The temporal evolution of the neutral species with 5% oxygen partial flow rate for Ar/O\(_2\) discharge with Ti target in poisoned mode.

Gudmundsson et al. (2016), PSST, accepted 2016
Ionization region model studies of reactive HiPIMS

- $\text{Ar}^+$ and $\text{Ti}^+$-ions dominate the discharge
- $\text{Ti}^{2+}$-ions follow by roughly an order of magnitude lower density
- The $\text{O}_2^+$ and $\text{O}^+$-ion density is much lower

The temporal evolution of the neutral species with 5% oxygen partial flow rate for Ar/O$_2$ discharge with Ti target in metal mode.

Gudmundsson et al. (2016), PSST, accepted 2016
Ar$^+$-ions dominate the discharge

Ti$^+$, O$^+$, have very similar density, but the temporal variation is different, and the O$_2^+$ density is slightly lower.

The Ti$^{2+}$-ion density increases fast with time and overcomes the Ti$^+$ density towards the end of the pulse.

The temporal evolution of the neutral species with 5% oxygen partial flow rate for Ar/O$_2$ discharge with Ti target in poisoned mode.

Gudmundsson et al. (2016), PSST, accepted 2016
Ar\textsuperscript{+} and Ti\textsuperscript{+}-ions contribute most significantly to the discharge current.

The temporal evolution of the neutral species with 5\% oxygen partial flow rate for Ar/O\textsubscript{2} discharge with Ti target in metal mode.

Gudmundsson et al. (2016), PSST, accepted 2016.
Ar\(^+\) contribute most significantly to the discharge current – almost solely.

The contribution of secondary electron emission is very small.

The temporal evolution of the neutral species with 5% oxygen partial flow rate for Ar/O\(_2\) discharge with Ti target in poisoned mode.

Gudmundsson et al. (2016), PSST, accepted 2016.
Recycling of ionized atoms coming from the target are required for the current generation in both modes of operation.

In the metal mode self-sputter recycling dominates and in the poisoned mode working gas recycling dominates.

The dominating type of recycling determines the discharge current waveform.

The temporal variations of the reaction rates for electron impact ionization of the argon atoms (ground state plus metastable) in poisoned mode.

Gudmundsson et al. (2016), PSST, accepted 2016.
In the metal mode sheath energization was found to be only 10 %
  
- same range as the results reported earlier for an Al target

For the poisoned mode the sheath energization was 30 %, with a rising trend, at the end of the pulse

This is due to the secondary electron emission

- In the poisoned mode essentially all the ions (mainly Ar$^+$, but also O$^+$ and Ti$^{2+}$ towards the end of the pulse) contribute to the secondary electron emission
- In the metal mode only half of the ions contribute to the secondary electron emission (Ar$^+$) while the other half does not contribute at all ($\gamma_{\text{Ti}^+} = 0.0$)
Summary
Summary

- An ionization region model was used to explore the plasma composition during the high power pulse.
- Comparison was made between the metal mode and the poisoned mode.
  - In metal mode $\text{Ar}^+$ and $\text{Ti}^+$-ions dominate the discharge and are of the same order of magnitude.
  - In poisoned mode $\text{Ar}^+$-ions dominate the discharge and two orders of magnitude lower, $\text{Ti}^+$, $\text{O}^+$, have very similar density, with the $\text{O}_2^+$ density slightly lower.
  - In the metal mode $\text{Ar}^+$ and $\text{Ti}^+$-ions contribute most significantly to the discharge current while in poisoned mode $\text{Ar}^+$ dominate.
- In the metal mode self-sputter recycling dominates and in the poisoned mode working gas recycling dominates – the dominating type of recycling determines the discharge current waveform.
The slides can be downloaded at
http://langmuir.raunvis.hi.is/~tumi/ranns.html

- The experimental work was made in collaboration with
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  - Tryggvi K. Tryggvason, University of Iceland

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  - Dr. Tomas Kubart, Uppsala University, Uppsala, Sweden

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