# An ionization region model of the reactive Ar/$O_2$ high power impulse magnetron sputtering discharge

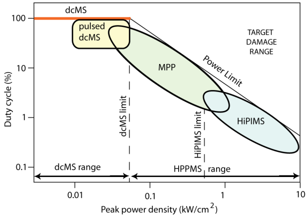
Jón Tómas Guðmundsson[1,2,3], Daniel Lundin[3], Michael A. Raadu[1], C. Huo[1], Nils Brenning[1] and Tiberu M. Minea[3]

[1] Department of Space and Plasma Physics, School of Electrical Engineering, KTH – Royal Institute of Technology, Stockholm, Sweden
[2] Science Institute, University of Iceland, Reykjavik, Iceland
[3] Laboratoire de Physique des Gaz et Plasmas - LPGP, UMR 8578 CNRS, Université Paris-Sud, 91405 Orsay Cedex, France
tumi@hi.is

69th Gaseous Electronics Conference, Bochum, Germany
October 11, 2016

# *Introduction*

- High ionization of sputtered vapor requires very high density plasma
- In a conventional dc magnetron discharge the power density (plasma density) is limited by the thermal load on the target
- High power pulsed magnetron sputtering (HPPMS)
- In a HiPIMS discharge a high power pulse is supplied for a short period
    - low frequency
    - low duty cycle
    - low average power

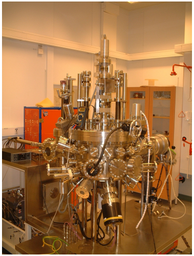



Gudmundsson et al. (2012), JVSTA **30** 030801

- Power density limits
  $p_t = 0.05$ kW/cm$^2$ dcMS limit
  $p_t = 0.5$ kW/cm$^2$ HiPIMS limit

## *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 $O_2$, $N_2$, or $CH_4$ etc. is mixed to the noble working gas for oxide, nitride, or carbide deposition
- HiPIMS deposition generally gives denser, smoother films og higher crystallinity than dcMS grown films



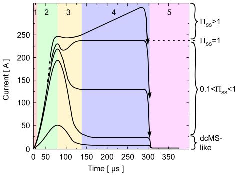
Helmersson et al. (2006) Thin Solid Films **513** 1

Magnus et al. (2012) IEEE EDL **33** 1045

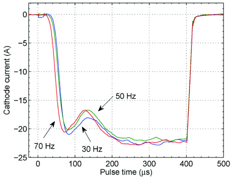
# HiPIMS - Voltage - Current - Time characteristics

# *HiPIMS - Voltage - Current - time*

- 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



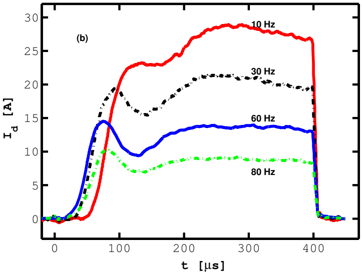

From Gudmundsson et al. (2012), JVSTA **30** 030801




From Magnus et al. (2011) JAP **110** 083306

# HiPIMS - Voltage - Current - time

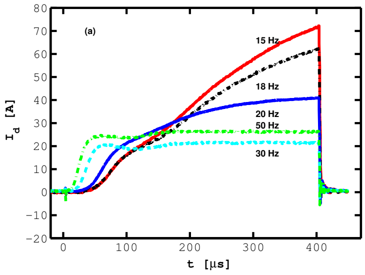
- During **reactive sputtering**, a reactive gas is added to the inert working gas
- The current waveform in the reactive Ar/$N_2$ HiPIMS discharge with Ti target is highly dependent on the pulse repetition frequency
- $N_2$ addition changes the plasma composition and the target condition can also change due to the formation of a compound on its surface




After Magnus et al. (2011) JAP **110** 083306

# *HiPIMS - Voltage - Current - time*

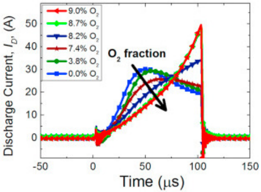
- Similarly for the Ar/$O_2$ discharge, the current waveform is highly dependent on the repetition frequency and applied voltage which is linked to oxide formation on the target
- The current is found to increase significantly as the frequency is lowered




After Magnus et al. (2012), JVSTA **30** 050601

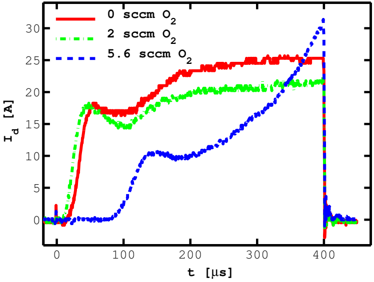
# HiPIMS - Voltage - Current - time

- As the oxygen flow is increased a transition to oxide mode is observed




The current waveforms for an $Ar/O_2$ discharge with a V target where the oxygen flow rate is varied

From Aijaz et al. (2016) Solar Energy Materials and Solar Cells **149** 137

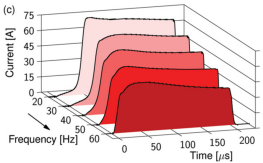


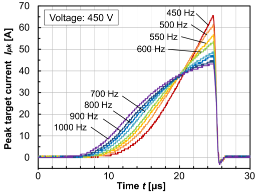

The current waveforms for an $Ar/O_2$ discharge with a Ti target where the oxygen flow rate is varied – 600 V, 50 Hz and 0.6 Pa

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

Gudmundsson (2016) Plasma Phys. Contr. Fus. **58** 014002

# HiPIMS - Voltage - Current - time




- 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

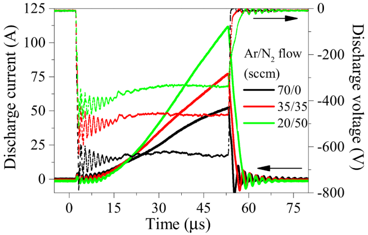
    From Shimizu et al. (2016), JPD **49** 065202

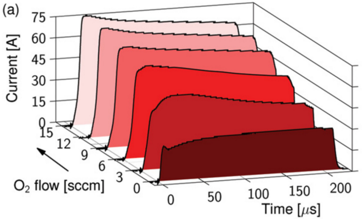
# *HiPIMS - Voltage - Current - time*

- The current increases with increased partial pressure of the reactive gas
  - The current waveform becomes distinctly triangular for Ar/$N_2$ discharge with Al target

    From Moreira et al. (2015), JVSTA **33** 021518
  - The current waveform maintains its shape for Ar/$O_2$ discharge with Nb target

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

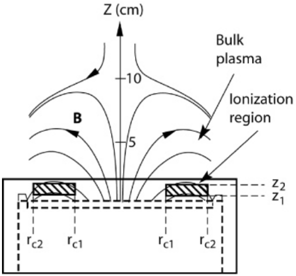


# Ionization region model studies of reactive HiPIMS

# *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




The definition of the volume covered by the IRM

From Raadu et al. (2011), PSST **20** 065007

# Ionization region model studies of reactive HiPIMS

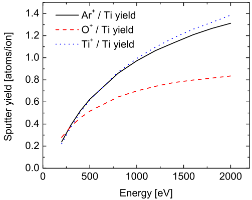
- The species assumed in the IRM are
  - electrons
  - argon atoms Ar($3s^2 3p^6$), warm argon atoms in the ground state $Ar^W$, hot argon atoms in the ground state $Ar^H$, $Ar^m$ ($1s_5$ and $1s_3$) (11.6 eV), argon ions $Ar^+$ (15.76 eV)
  - titanium atoms Ti($a\,^3F$), titanium ions $Ti^+$ (6.83 eV), doubly ionized titanium ions $Ti^{2+}$ (13.58 eV)
  - oxygen molecule in the ground state $O_2(X^3\Sigma_g^-)$, the metastable oxygen molecules $O_2(a^1\Delta_g)$ (0.98 eV) and $O_2(b^1\Sigma_g)$ (1.627 eV), the oxygen atom in the ground state $O(^3P)$, the metastable oxygen atom $O(^1D)$ (1.96 eV), the positive ions $O_2^+$ (12.61 eV) and $O^+$ (13.62 eV), and the negative ion $O^-$

Toneli et al. (2015) J. Phys. D. **48** 325202

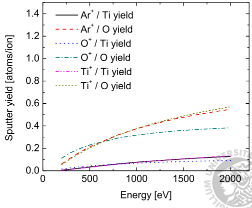
# *Ionization region model studies of reactive HiPIMS*

- 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

(a)



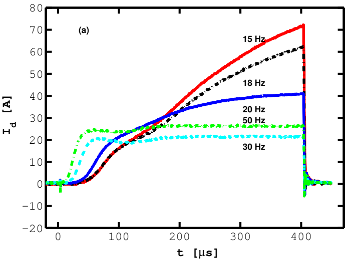

(b)




The sputter yield data is from Tomas Kubart, Uppsala University

# *Ionization region model studies of reactive HiPIMS*

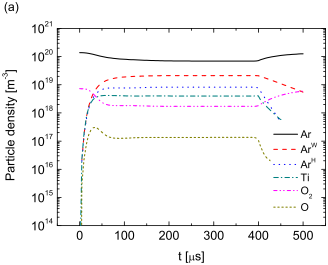
- The model is applied to explore Ar/$O_2$ discharge with Ti target in both metal mode and oxide (poisoned) mode
- The IRM is a semi-empirical model in the sense that it uses a measured discharge current waveform as a main input parameter
- For this study we use the measured curve for Ar/$O_2$ with Ti target at 50 Hz for metal mode and at 15 Hz for poisoned mode




After Magnus et al. (2012), JVSTA **30** 050601

# *Ionization region model studies of reactive HiPIMS*

- The gas rarefaction is observed for the argon atoms but is more significant for the $O_2$ molecule
- The density of Ti atoms is higher than the $O_2$ density
- The atomic oxygen density of is over one order of magnitude lower than the molecular oxygen density – the dissociation fraction is low

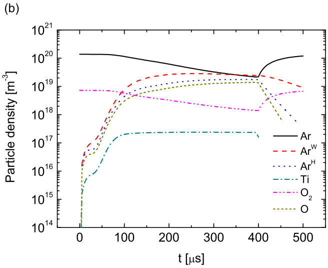



The temporal evolution of the neutral species with **5 % oxygen partial flow** rate for Ar/$O_2$ discharge with Ti target in **metal mode**.

Gudmundsson et al. (2016), PSST, 25(6) 065004

# *Ionization region model studies of reactive HiPIMS*

- Gas rarefaction is observed for both argon atoms and $O_2$ molecules
- The density of Ti atoms is lower than both the $O_2$ density and atomic oxygen density
- The atomic oxygen density is higher than the $O_2$ density towards the end of the pulse



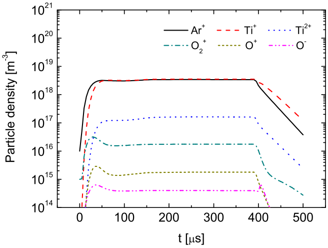

The temporal evolution of the neutral species with **5 % oxygen partial flow** rate for Ar/$O_2$ discharge with Ti target in **poisoned mode**.

Gudmundsson et al. (2016), PSST, 25(6) 065004

# *Ionization region model studies of reactive HiPIMS*

- $Ar^+$ and $Ti^+$-ions dominate the discharge
- $Ti^{2+}$-ions follow by roughly an order of magnitude lower density
- The $O_2^+$ and $O^+$-ion density is much lower

(a)



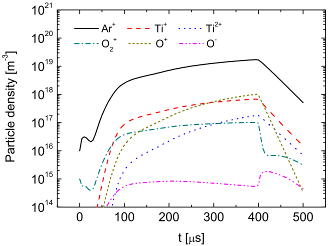

The temporal evolution of the neutral species with **5 % oxygen partial flow** rate for Ar/$O_2$ discharge with Ti target in **metal mode**.

Gudmundsson et al. (2016), PSST, 25(6) 065004

# Ionization region model studies of reactive HiPIMS

- $Ar^+$-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

(b)

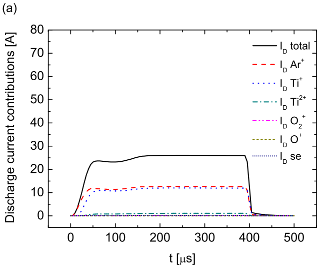



The temporal evolution of the neutral species with **5 % oxygen partial flow** rate for Ar/$O_2$ discharge with Ti target in **poisoned mode**.

Gudmundsson et al. (2016), PSST, 25(6) 065004

# *Ionization region model studies of reactive HiPIMS*

- $Ar^+$ and $Ti^+$-ions contribute most significantly to the discharge current

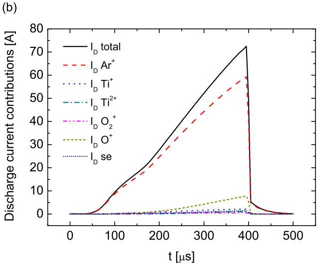



The temporal evolution of the neutral species with **5 % oxygen partial flow** rate for Ar/$O_2$ discharge with Ti target in **metal mode**.

Gudmundsson et al. (2016), PSST, 25(6) 065004

# *Ionization region model studies of reactive HiPIMS*

- $Ar^+$ contribute most significantly to the discharge current – almost solely
- The contribution of secondary electron emission is very small

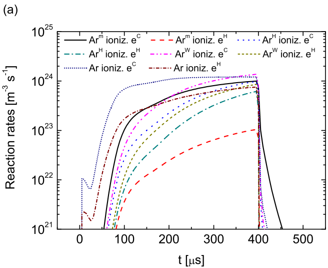



The temporal evolution of the neutral species with **5 % oxygen partial flow** rate for $Ar/O_2$ discharge with Ti target in **poisoned mode**.

Gudmundsson et al. (2016), PSST, 25(6) 065004

# *Ionization region model studies of reactive HiPIMS*

- 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, 25(6) 065004

# *Ionization region model studies of reactive HiPIMS*

- In the metal mode sheath energization was found to be only 10 %
  - same range as the results reported earlier for an Al target

    Huo et al. (2013), PSST **22**(4) (2013) 045005
- 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 ($\gamma_{Ti^+} = 0.0$)

# 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 $Ar^+$ and $Ti^+$-ions dominate the discharge and are of the same order of magnitude
  - In poisoned mode $Ar^+$-ions dominate the discharge and two orders of magnitude lower, $Ti^+$, $O^+$, have very similar density, with the $O_2^+$ density slightly lower
  - In the metal mode $Ar^+$ and $Ti^+$-ions contribute most significantly to the discharge current while in poisoned mode $Ar^+$ 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
  - Dr. Fridrik Magnus, Uppsala University, Uppsala, Sweden
  - Tryggvi K. Tryggvason, University of Iceland
- We got help with the sputtering yields from
  - Dr. Tomas Kubart, Uppsala University, Uppsala, Sweden
- and the project is funded by
  - Icelandic Research Fund Grant No. 130029-053
  - Swedish Government Agency for Innovation Systems (VINNOVA) contract no. 2014-04876,

# References

Aijaz, A., Y.-X. Ji, J. Montero, G. A. Niklasson, C. G. Granqvist, and T. Kubart (2016). Low-temperature synthesis of thermochromic vanadium dioxide thin films by reactive high power impulse magnetron sputtering. *Solar Energy Materials and Solar Cells 149*, 137–144.

Aiempanakit, M., A. Aijaz, D. Lundin, U. Helmersson, and T. Kubart (2013). Understanding the discharge current behavior in reactive high power impulse magnetron sputtering of oxides. *Journal of Applied Physics 113*(13), 133302.

Gudmundsson, J. T. (2016). On reactive high power impulse magnetron sputtering. *Plasma Physics and Controlled Fusion 58*(1), 014002.

Gudmundsson, J. T., N. Brenning, D. Lundin, and U. Helmersson (2012). The high power impulse magnetron sputtering discharge. *Journal of Vacuum Science and Technology A 30*(3), 030801.

Gudmundsson, J. T., F. Magnus, T. K. Tryggvason, S. Shayestehaminzadeh, O. B. Sveinsson, and S. Olafsson (2013). Reactive high power impulse magnetron sputtering. In *Proceedings of the XII International Symposium on Sputtering and Plasma Processes (ISSP 2013)*, pp. 192–194.

Gudmundsson, J. T., D. Lundin, N. Brenning, M. A. Raadu, C. Huo, and T. M. Minea (2016). An ionization region model of the reactive Ar/$O_2$ high power impulse magnetron sputtering discharge. *Plasma Sources Science and Technology 25*(6), 065004.

Hála, M., J. Čapek, O. Zabeida, J. E. Klemberg-Sapieha, and L. Martinu (2012). Hysteresis - free deposition of niobium oxide films by HiPIMS using different pulse management strategies. *Journal of Physics D: Applied Physics 45*(5), 055204.

Helmersson, U., M. Lattemann, J. Bohlmark, A. P. Ehiasarian, and J. T. Gudmundsson (2006). Ionized physical vapor deposition (IPVD): A review of technology and applications. *Thin Solid Films 513*(1-2), 1–24.

# References

Huo, C., D. Lundin, M. A. Raadu, A. Anders, J. T. Gudmundsson, and N. Brenning (2013). On sheath energization and ohmic heating in sputtering magnetrons. *Plasma Sources Science and Technology 22*(4), 045005.

Magnus, F., A. S. Ingason, S. Olafsson, and J. T. Gudmundsson (2012). Nucleation and resistivity of ultrathin TiN films grown by high power impulse magnetron sputtering. *IEEE Electron Device Letters 33*(7), 1045 – 1047.

Magnus, F., O. B. Sveinsson, S. Olafsson, and J. T. Gudmundsson (2011). Current-voltage-time characteristics of the reactive Ar/$N_2$ high power impulse magnetron sputtering discharge. *Journal of Applied Physics 110*(8), 083306.

Magnus, F., T. K. Tryggvason, S. Olafsson, and J. T. Gudmundsson (2012). Current-voltage-time characteristics of the reactive Ar/$O_2$ high power impulse magnetron sputtering discharge. *Journal of Vacuum Science and Technology A 30*(5), 050601.

Moreira, M. A., T. Törndahl, I. Katardjiev, and T. Kubart (2015). Deposition of highly textured AlN thin films by reactive high power impulse magnetron sputtering. *Journal of Vacuum Science and Technology A 33*(2), 021518.

Raadu, M. A., I. Axnäs, J. T. Gudmundsson, C. Huo, and N. Brenning (2011). An ionization region model for high power impulse magnetron sputtering discharges. *Plasma Sources Science and Technology 20*(6), 065007.

Shimizu, T., M. Villamayor, D. Lundin, and U. Helmersson (2015). Process stabilization by peak current regulation in reactive high-power impulse magnetron sputtering of hafnium nitride. *Journal of Physics D: Applied Physics 49*(6), 065202.

Toneli, D. A., R. S. Pessoa, M. Roberto, and J. T. Gudmundsson (2015). On the formation and annihilation of the singlet molecular metastables in an oxygen discharge. *Journal of Physics D: Applied Physics 48*(32), 325202.