Particle-balance models for pulsed sputtering magnetrons: The role of recycling

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Introduction

- Magnetron sputtering has been the workhorse of plasma based sputtering methods for almost five decades
- Magnetron sputtering discharges are widely used in thin film processing

Applications include
- thin films in integrated circuits
- magnetic material
- hard, protective, and wear resistant coatings
- optical coatings
- decorative coatings
- low friction films
Introduction

- A magnet is placed at the back of the cathode target with the pole pieces at the center and perimeter.
- The magnetic field confines the energetic electrons near the cathode, where they undergo numerous ionizing collisions before being lost to a grounded surface.
- If the cathode plate is circular, the magnetic confinement is seen as a torus shaped plasma that hovers in front of the target.
Introduction

Through the years there has been a continuous development of the magnetron sputtering processes to

- increase the ionization of the sputtered vapor
- improve target utilization
- avoid target poisoning in reactive sputtering

For many applications a high degree of ionization of the sputtered vapor is desired

- controlled ion bombardment of the growing film
- ion energy can be controlled by a negative bias applied to the substrate
- collimation – enhanced step coverage
Introduction

- High ionization of sputtered material requires very high density plasma
- In a conventional dc magnetron sputtering 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

\[ p_t = 0.05 \text{ kW/cm}^2 \text{ dcMS limit} \]
\[ p_t = 0.5 \text{ kW/cm}^2 \text{ HiPIMS limit} \]
Introduction

- Temporal and spatial variation of the electron density
- Ar discharge at 20 mTorr, Ti target, pulse length 100 $\mu$s
- The electron density in the substrate vicinity is of the order of $10^{18} - 10^{19} \text{ m}^{-3}$ – ionization mean free path $\lambda_{iz} \sim 1 \text{ cm}$
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 and higher crystallinity than dcMS grown films.

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

Magnus et al. (2012) IEEE EDL 33 1045
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Reactive HiPIMS - Applications
Application – Film Resistivity

- TiN as diffusion barriers for copper and aluminum interconnects
- HiPIMS deposited films have significantly lower resistivity than dcMS deposited films on SiO$_2$ at all growth temperatures due to reduced grain boundary scattering
- Thus, ultrathin continuous TiN films with superior electrical characteristics and high resistance towards oxidation can be obtained with HiPIMS at reduced temperatures

From Magnus et al. (2012) IEEE EDL 33 1045
**Application – Bragg mirror**

- Multilayer structures containing a high-contrast (TiO$_2$/SiO$_2$) Bragg mirror
- fabricated on fused-silica substrates
  - reactive HiPIMS TiO$_2$ (88 nm)
  - reactive dcMS SiO$_2$ (163 nm)
  - capped with semitransparent gold
- Rutile TiO$_2$ ($n = 2.59$) and SiO$_2$ ($n = 1.45$) provide a large index contrast
- Smooth rutile TiO$_2$ films can be obtained by HiPIMS at relatively low growth temperatures, without post-annealing


Agnarsson et al. (2013) TSF 545 445
Voltage - Current - Time characteristics

Non-reactive HiPIMS
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 has a contribution from the working gas ions, whereas the later phase has a strong contribution from self-sputtering at high voltage.

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

From Magnus et al. (2011) JAP 110 083306
Ionization region model studies of non-reactive HiPIMS
Ionization region model non-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 temporal development is defined by a set of ordinary differential equations giving the first time derivatives of
- the electron energy
- the particle densities for all the particles

The species assumed in the non-reactive-IRM are
- electrons
- argon atoms Ar(3s^23p^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)
- aluminium atoms Al(^2P_{1/2}), aluminium ions Al^+ (5.99 eV), doubly ionized aluminium ions Al^{2+} (18.8 eV)

Detailed model description is given in Huo et al. (2017), JPD submitted 2017
The model is constrained by experimental data input and fitted to reproduce the measured discharge current and voltage curves, $I_D(t)$ and $U_D(t)$, respectively.

Two model fitting parameters were found to be sufficient for a discharge with Al target:

- $U_{IR}$ accounts for the power transfer to the electrons
- $\beta$ is the probability of back-attraction of ions to the target

From Huo et al. (2017), JPD submitted 2017

Experimental data from Anders et al. (2007) JAP 102 113303
A non-reactive discharge with Al target

When the discharge is operated at 400 V the contributions of Al$^+$ and Ar$^+$-ions to the discharge current are very similar.

At 800 V Al$^+$-ions dominate the discharge current (self-sputtering) while the contribution of Ar$^+$ is below 10 % except at the initiation of the pulse.

From Huo et al. (2017), JPD submitted 2017

Experimental data from Anders et al. (2007) JAP 102 113303
A non-reactive discharge with Ti target

The contributions to the discharge current for two cases, weak (180 Gauss) and strong (380 Gauss) magnetic field, at 75 Hz pulse frequency

Stronger magnetic field leads to a higher discharge current

Higher magnetic field strength leads to higher relative contribution of Ti$^{2+}$ while it lowers the relative contribution of Ti$^+$

From Huo et al. (2017), JPD submitted 2017

Experimental data from Bradley et al. (2015) JPD 48 215202
Ionization region model non-reactive HiPIMS

- A primary current $I_{\text{prim}}$ is defined as ions of the working gas, here $\text{Ar}^+$, that are ionized for the first time and then drawn to the target.
- This is the dominating current in dc magnetron sputtering discharges.
- This current has a critical upper limit

$$I_{\text{crit}} = S_R T e \rho g \sqrt{\frac{1}{2\pi m_g k_B T_g}} = S_R T e n_g \sqrt{\frac{k_B T_g}{2\pi m_g}}$$

- Discharge currents $I_D$ above $I_{\text{crit}}$ are only possible if there is some kind of recycling of atoms that leave the target, become subsequently ionized and then are drawn back to the target.

Anders et al. (2012), JPD 45 012003
Huo et al. (2014), PSST 23 025017
For the Al target the critical current is $I_{\text{crit}} \approx 7 \text{ A}$

The experiment is operated from far below $I_{\text{crit}}$ to high above it, up to 36 A.

With increasing current $I_{\text{prim}}$ gradually becomes a very small fraction of the total discharge current $I_D$

The current becomes mainly carried by singly charged $\text{Al}^+$ ions, meaning that the current $I_{\text{SS-recycle}}$ or self-sputter recycling dominates.
The discharge with the Ti target is operated with peak current far above the critical current of $I_{\text{crit}} \approx 19$ A.

This discharge shows close to a 50/50 combination of **self-sputter recycling** $I_{\text{SS-recycle}}$ and **working gas-recycling** $I_{\text{gas-recycle}}$.

From Huo et al. (2017), JPD submitted 2017

Experimental data from Bradley et al. (2015) JPD 48, 215202
Recall that singly charged metal ions cannot create the secondary electrons – for metal self-sputtering ($\gamma_{SE}$ is practically zero).

The first ionization energies of many metals are insufficient to overcome the workfunction of the target material.

For the discharge with Al target operated at high voltage, self-sputter dominated, the effective secondary electron emission is close to zero.
The power transfer to the electrons is given by

\[ P_e = P_{SH} + P_{Ohm} = I_{e,SH} (U_D - U_{IR}) + \frac{I_D U_{IR}}{2} \]

where

\[ P_{SH} = I_{e,SH} U_{SH} = \left( I_{Ar^+} \gamma_{Ar^+,eff} + \frac{1}{2} I_{M^2+} \gamma_{M^2+,eff} \right) U_{SH} \]

and

\[ P_{Ohm} = I_{e,IR} U_{IR} = \left\langle \frac{J_e}{J_D} \right\rangle I_D U_{IR} \]

Then

\[ I_{e,SH} \sim \gamma_{SE} \epsilon_e m (1 - r) I_D \sim 0.05 I_D \text{ and } I_{e,SH} \ll I_D/2 \text{ so that} \]

\[ I_{e,SH} \ll I_D/2 \]

and Ohmic heating is more efficient.
For the Al target, the fraction of the total electron heating that is attributable to Ohmic heating is found in the range of 0.87 (360 V) to 0.99 (1000 V).

The domination of Al\(^+\)-ions, which have zero secondary electron emission yield, has the consequence that there is negligible sheath energization.

The ionization threshold for twice ionized Al\(^{2+}\), 18.8 eV, is so high that few such ions are produced.

From Huo et al. (2017), JPD submitted 2017
For the discharge with Ti target more $\text{Ar}^+\text{-ions}$ contribute to the current and the ionization degree of Ti$^{2+}$ is more than order of magnitude larger than the ionization degree of Al$^{2+}$, so there are more secondary electrons

- The fraction of the total electron heating that is attributable to Ohmic heating is about 0.92

- Decreasing the magnetic field strength (BF1 to BF4) slightly reduces the Ohmic heating fraction
Ionization region model non-reactive HiPIMS

- The model results show that for an argon discharge with Al target the contribution of Al$^+$-ions is over 90% at 800 V, while Al$^+$-ions and Ar$^+$-ions contribute roughly equally to the discharge current at 400 V.
- For high currents the discharge with Al target develops almost pure **self-sputter recycling**, while the discharge with Ti target exhibits close to a 50/50 combination of **self-sputter recycling** and **working gas-recycling**.
- For a Ti target, a self-sputter yield significantly below unity makes working gas-recycling necessary at high currents.
- The model results show that Al$^{2+}$-ions contribute negligibly, while Ti$^{2+}$-ions effectively contribute to the production of secondary electrons.
- The fraction of the total electron heating that is attributable to Ohmic heating is over 90%.
Voltage - Current - Time characteristics

Reactive HiPIMS
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
Particle-balance models for pulsed sputtering magnetrons: The role of recycling

**HiPIMS - Voltage - Current - time**

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

![Graph](image)

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

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
The current increases with increased partial pressure of the reactive gas

- The current waveform becomes distinctly triangular for Ar/N₂ discharge with Al target
  From Moreira et al. (2015), JVSTA 33 021518

- The current waveform maintains its shape for Ar/O₂ discharge with Nb target
  From Hála et al. (2012), JPD 45 055204
Particle-balance models for pulsed sputtering magnetrons: The role of recycling

Ionization region model studies of reactive HiPIMS
Ionization region model studies of reactive HiPIMS

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

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
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 voltage and current waveforms 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$_2$ molecule.

The density of Ti atoms is higher than the O$_2$ density.

The atomic oxygen density 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.
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
The increase in the atomic oxygen in the ground state is due to:

- sputtering of O($^3P$) from the partially to fully oxidized target (dominates)
- electron impact de-excitation of O($^1D$)
- electron impact dissociation of the O$_2$ ground state molecule

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

Lundin et al. (2017), JAP, 121(17) 171917
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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 $\text{Ar}/\text{O}_2$ discharge with Ti target in metal mode.

Gudmundsson et al. (2016), PSST, 25(6) 065004
Ionization region model studies of reactive HiPIMS

- $\text{Ar}^+$-ions dominate the discharge
- $\text{Ti}^+$, $\text{O}^+$, have very similar density, but the temporal variation is different, and the $\text{O}_2^+$ density is slightly lower
- The $\text{Ti}^{2+}$-ion density increases fast with time and overcomes 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, 25(6) 065004
Ionization region model studies of reactive HiPIMS

- Ar\(^+\) and Ti\(^+\)-ions contribute most significantly to the discharge current at the cathode target surface – almost equal contribution
- \(I_{\text{crit}} \approx 5\) 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
Particle-balance models for pulsed sputtering magnetrons: The role of recycling

Ionization region model studies of reactive HiPIMS

- $Ar^+$ contribute most significantly to the discharge current – almost solely – at the cathode target surface
- The contribution of secondary electron emission is very small
- $I_{\text{crit}} \approx 5 \, \text{A}$

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
Towards the end of the pulse more than half of the Ar$^+$-ions are created from argon atoms that come from the target

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

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

- The sum of the ionization rates for the $e^C$ plus the $e^H$ populations, and that for the $e^H$ electron population alone.
- Here both the metal and the poisoned mode are shown.
- The hot electron reactions are more important in the poisoned mode.

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

Gudmundsson et al. (2016), PSST, 25(6) 065004
Recycling of atoms coming from the target and then ionized 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
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) 045005

the dominating electron heating mechanism is Ohmic heating

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 (γ\(^{Ti^+}\) = 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
Thank you for your attention

The slides can be downloaded at
http://langmuir.raunvis.hi.is/~tumi/ranns.html

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References


References


