High-Power Impulse Magnetron Sputtering for the synthesis of functional metal oxide thin films

stephanos.konstantinidis@umons.ac.be
Our « philosophy »

- Working parameters
  - Electric power \( I(t) \& V(t) \)
  - Pressure
  - Gas mixture
  - Chamber geometry

- Plasma physics & chemistry
  - Energies
  - Densities

- Plasma – Surface Interactions
  - Energy deposition
  - Surface diffusion
  - Implantation

- Surface properties
  - Film growth mechanisms
  - Elemental composition
  - Phase constitution
  - Density

- Applications
  - Corrosion & wear resistance
  - Photocatalysis
  - Photovoltaics
  - Biocompatibility
  - ...
1) High Power Impulse Magnetron Sputtering, why and how?

2) **What happens** if HiPIMS is used for the synthesis of transition metal oxide thin films?
Conventional DC magnetron sputter deposition

CATHODE
(Negative potential)

METAL Target

Substrate
Target surface chemistry changes with O$_2$ partial pressure
Magnetron sputtering in the Industry

https://invest.dresden.de/
Filling holes by magnetron sputtering

...problem !
The solution:
Let’s ionize the sputtered metal atoms
Advantages brought by the ionization of the sputtered metal atoms

Metal ions (+ negative bias on the substrate) allows:

1. Controlling the trajectory of the film – forming species
   – Conformal deposition

2. Controlling the kinetic energy of the film – forming species
   – Crystallinity, micro/nanostructure, roughness,... are modified

How can we do that?

• Promote ionization by electron impact
• «Heat» the electrons of the plasma
The power supply delivers:

- **Voltage up to 1 – 2 kV**
- **Peak current in the range of 10-100 of Amps**

Pulsed discharge to avoid overheating the target/magnets
Typical Current-Voltage-Time waveforms

Conventional DCMS
Current - Voltage - Time waveforms
The HiPIMS plasma

M + e⁻ → M⁺ + 2e⁻
Production of ionized metal atoms


Film – forming species with high kinetic energies

DC Magnetron

HiPIMS

Plasma dynamics

Time & space – dependent plasma chemistry

Pulse - 20 μs
Period - 1 ms
Pressure - 20 mTorr

$^{1+}$Ar met  Ti  Ti$^+$

000 μs

Magnetron cathode

Towards a definition of HiPIMS

1. Magnetron plasma
   – Glow discharge in ExB fields

2. Electric pulses
   – Duty cycle ≤ 1%

3. High power/peak current
   1. ~kW / A cm⁻²
   2. ⇒ \( N_e \sim 10^{12-13} \text{ cm}^{-3} \)

4. High ionization rate of the sputtered material

Conformal deposition on complex-shape objects


Alami et al, JVST A (2007)
Some more knobs to tune film properties

- Energy deposition during film growth

- More knobs for tuning the thin film properties
  - Pressure & gas mixture
  - Magnetic & chamber geometry
  - Average power
  - Pulse duration & frequency
  - Pulse voltage
On the synthesis of metal oxide thin films by HiPIMS

1. Titanium dioxide
2. Aluminum-doped zinc oxide
3. Vanadium dioxide
Titanium dioxide
Growing high-temperature phase of TiO$_2$ by HiPIMS

Modulating the phase constitution through peak power

![Intensity vs. 2θ chart]

Too high ion flux may lead to amorphization

CrN films

Increased refractive index of TiO$_2$ films

Anatase films deposited on glass

Increased compactness

Deposition of photocatalytic TiO$_2$ onto polymers

Fig. 5. First rate order constant value for the process of photodegradation of MB as a function of sputtering parameters (pressure, pulse width, pulse frequency).

Fig. 7. First rate order constant value for the process of photodegradation of MB of the coatings deposited onto various substrate types under optimised conditions.

Al-doped ZnO
Transmittance of Al-doped ZnO

Sputtering from an alloy target (Zn+Al) in Ar/O₂ atmosphere

Deposition at room temperature

Electric properties of ZnO:Al

HiPIMS leads to:
- Low resistivity ($10^{-4} \ \Omega \ cm$)
- Spatial homogeneity

Table S2: Hall effect measurement results of the AZO film deposited using HiPIMS at 570 V

<table>
<thead>
<tr>
<th>Position (cm)</th>
<th>Resistivity (Ωcm)</th>
<th>Mobility (cm$^2$/Vs)</th>
<th>Charge carrier concentration (cm$^{-3}$)</th>
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<tbody>
<tr>
<td>3</td>
<td>$2.05 \times 10^{-3}$</td>
<td>4.09</td>
<td>$7.47 \times 10^{20}$</td>
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<tr>
<td>4</td>
<td>$7.50 \times 10^{-4}$</td>
<td>7.38</td>
<td>$1.13 \times 10^{21}$</td>
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<td>5</td>
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<td>10.5</td>
<td>$8.24 \times 10^{20}$</td>
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<td>6</td>
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<tr>
<td>7</td>
<td>$1.23 \times 10^{-3}$</td>
<td>8.84</td>
<td>$5.76 \times 10^{20}$</td>
</tr>
</tbody>
</table>

Vanadium dioxide
Synthesis of thermochromic VO$_2$ at low temperature


Similar results were obtained by
Recent developments in HiPIMS technology

1. Peak current controlled reactive HiPIMS
2. Bipolar HiPIMS
Peak current controlled R-HiPIMS

Controlling discharge conditions, working inside the unstable transition zone

Ar:100sccm, 1.3Pa
$U_c = 610$V, $O_2$:1sccm

Metallic

Poisoned
Bipolar HiPIMS controlling ion energy without the need of a substrate bias

Ion energy is controlled by the positive voltage


M. Michiels et al, manuscript in preparation
TiO$_2$ by Bipolar HiPIMS on glass substrates

M. Michiels et al, manuscript in preparation
Influence of positive voltage on the properties of DLC coatings

Summary

1. HiPIMS promotes intense ion bombardment during deposition which modifies the growth process and film properties
   - Increased density
   - Modified crystallinity (high-temp. phase, texture, crystallite size)
   - Lower roughness

2. HiPIMS may facilitate the deposition of functional oxides onto temperature sensitive materials like polymers

3. Recent developments aim at providing even more control on the film growth process
In Mons, we don’t have dears but we have a dragon