Coating Properties of Cu and TiO$_2$ on Polymer Web Deposited by High Power Impulse Magnetron Sputtering With Positive Voltage Reversal and Pulsed DC

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Coatings on polymer web can be challenging due to temperature limitations and the fact that most polymers are electrically insulating.

Demands from the market for better control over coating properties such as density and optical and electrical properties.

Need a means to add energy to the growing film without damaging the substrate.

Need a technology which can be easily implemented/retrofitted into a roll to roll coater.
Copper and TiO2 chosen to look at film structure, electrical and optical properties

Copper is a high mobility material used in flexible electronics. Control over grain size is critical for thin films with regards to resistivity.

TiO2 is a low mobility and high index of refraction material widely used for optical coatings. Film density and crystallinity are important.

Will examine: film microstructure, grain size, resistivity, index of refraction, crystal structure

Comparison of DC, Pulsed DC and HIPIIMS with positive voltage reversal magnetron sputtering
Intellivation Company Overview

- Roll to roll coating system manufacturer located in Fort Collins, Colorado
  - Founded in 2009

- Web widths from 0.050m to 2m

- Specializing in multi-zone sputter deposition coating tools

- On-site Application Lab for R&D, demonstrations

- Configurable systems designed to support a wide range of high end applications
Opened in 2017.

Dedicated to customer demonstrations and internal R&D.

Featuring the R2R330 machine
- 4 Coating zones
- 330mm [13”] coated width

Single and dual rotary magnetrons were used for this work.

Modules are available for thermal evaporation, e-beam evaporation, sublimation, CVD, and PECVD.
Nano4Energy Company Overview

HIPIIMS power supplies with Positive Voltage Reversal
Coating development
Contract R&D
On site process implementation
Founded 2012
Located in Madrid, Spain

hip-V Power Supplies

1, 6, 10 and 20kW
Unipolar / Bipolar
Standard / Positive Voltage Reversal
Can be stacked up to 80 kW
Synchronized pulsing/bias

Developed and produced by Viesca Engineering
Founded 2004
Producer of high power pulsed power supplies for trains
HIPIMS intro

- High peak powers (500-2000 W/cm²)
- Reasonable average power (up to 80kW)
- Low duty factors (0.5-5%)
HIPIMS intro

Active V+

Passive V+

no V+

HiPlus

HIPIMS intro

Active V+

Passive V+

no V+

HiPlus
HIPIMS intro

- Ion acceleration from the target surface (0-1000 eV)
- Raise of plasma potential (bombardment of low V surfaces)

\[ E_i = E_0 + Qe \left( V_{\text{plasma}} - V_{\text{surface}} \right) \]
Background lit Cu

**Cu Resistivity: Effect of Surface and Grain Boundary Scattering**

- **Surface Scattering**
  - Fuchs-Sondheimer model
  
  \[ \rho_{\text{surf}} = \rho(h, w, p, \lambda) \]
  
  - \( h, w \): conductor height and width
  - \( p \): specularly parameter
  - \( \lambda \): electron mean free path

- **Grain Boundary Scattering**
  - Mayoada-Shatzkes model
  
  \[ \rho_{\text{g.b.}} = \rho(d, R, \lambda) \]
  
  - \( d \): ave. grain boundary distance
  - \( R \): Reflection coefficient at g.b.
  - \( \lambda \): electron mean free path

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**Thin Film Resistivity: Role of Carrier Scattering**

- **Effect of Electron Scattering**
  - Reduced mobility as dimensions decrease
  - Grain boundary scattering
  - Surface scattering
  - Reduced mobility as chip temperature increases
  - Increased phonon scattering

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Khojier et al., Int. J Nano Dimens. 3(3), 217-226, Winter 2013
Background lit TiO2

- Polymorphous material
  - Amorphous, anatase and rutile forms found with PVD
  - Anatase coatings are important for photocatalytic coatings for self cleaning and anti-bacterial surfaces
  - Rutile coatings have high transparency and refractive index making them attractive for low emissivity and anti-reflective coatings

- DCMS coatings are typically amorphous at room temperature.*
  - At temperatures up to 600°C, anatase is formed
  - Above 600°C, rutile phase forms

- Index of refraction is important for optical stacks

- No reported work in literature using a TiOx target and HIPIMS, only reactive sputtering from a Ti target.

*Agnarsson et al., Thin Solid Films, 2013
General Experimental Conditions

- Rotary magnetrons and 3mT Argon environment were used in all cases [oxygen added where noted].
- Discrete substrates were coated while affixed to the coating drum.
- Substrates included BK7 glass microscope slides, silicon wafers, quartz, and 5mil PET.
- All coating was dynamic in nature, mimicking continuous roll to roll processing. Multiple coating passes were utilized to control thermal load.
- Coating drum temperature was maintained at approximately 75F [24C].
Experimental Conditions Cu

- Cu target, 100 mm OD x 600 mm length
- Estimated racetrack area – 600 cm²
- 5 kW average power
- 3 mtorr
- Single magnetron with chamber as anode
- Single pass for thin films
- Multiple passes to get thick films
- Power
  - Pulsed DC
  - HIPIIMS 100 μs/625 V/100 A/100 V positive voltage reversal
    100 μs/645 V/180 A/250 V positive voltage reversal
    100 μs/670 V/350 A/328 V positive voltage reversal
Cu Dynamic Deposition Rate

![DC Normalized Dynamic Deposition Rate Chart]

- DC
- Pulsed DC
- H100
- H180
- H350

\[
\text{Ar}^+ \quad \text{Me}^+ \quad \text{Me}^+ \quad \text{Me}^+
\]
Cu Data SEM

DC  Pulsed DC  MFAC  Hipims 100A  Hipims 180A  Hipims 350A
Cu Data Resistivity

Resistivity versus Condition - Glass Substrate

Resistivity versus Condition - PET Substrate

Bulk Cu
Cu grain size

Straight DC
Grain size ~ 22nm

HiPIMS 400A
Grain size ~ 15nm
Experimental Conditions TiO2

- TiOx target, 5kW average power, 5.0 sccm of additional O2 flow
- Single magnetron with chamber as anode
- Multiple passes to get thick films
- Power
  - Pulsed DC
  - HIPIMS 60 μs/600V/200 A/300 V positive voltage reversal
  - 40 μs/670V/400 A/350 V positive voltage reversal
TiO₂ Dynamic Deposition Rate

DC Normalized Dynamic Deposition Rate

- Pulsed DC
- H₂O
- H₄O
TiO2 Morphology

- Pulsed DC
- HiPIMS 200A, +350V
- HiPIMS 400A, +400V

956 nm

800 nm

591 nm
TiO2 XRD

XRD

- Si
- H400
- H200
- Pulsed DC

2 theta

Intensity (AU)
TiO$_2$ Optical

- **Pulsed DC**
  - $n = 2.07$

- **Hipims 200A**
  - $n = 2.26$

- **Hipims 400A**
  - $n = 2.32$
Thermal Measurements

- Thermocouples were attached to the coating drum, and 1/2mil [12micron] PET substrate was threaded over them. Coating took place in R2R mode with web tension applied.

- Equal thickness coatings were applied in a single pass with one magnetron using each power supply.
  - Copper Thickness: 50nm
  - TiO2 Thickness: 10nm

- The presence of the thermocouple significantly disrupts the heat transfer mechanisms, and the thermocouple is not directly attached to the substrate. The measurements are comparative in nature, rather than absolute measurements of the substrate temperature.
Thermal Measurements

- The temperature rise for each power supply type was recorded, and the rise per nanometer of coating thickness applied has been calculated.
Thermal Loading - Cu

**Temperature Rise Single Pass - Cu**

<table>
<thead>
<tr>
<th></th>
<th>Temperature Rise (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC</td>
<td>15</td>
</tr>
<tr>
<td>Pulsed DC</td>
<td>15</td>
</tr>
<tr>
<td>H100</td>
<td>20</td>
</tr>
<tr>
<td>H280</td>
<td>25</td>
</tr>
<tr>
<td>H350</td>
<td>30</td>
</tr>
</tbody>
</table>

**Temperature Rise/nm**

<table>
<thead>
<tr>
<th></th>
<th>Temperature Rise (°C/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC</td>
<td>0.10</td>
</tr>
<tr>
<td>Pulsed DC</td>
<td>0.10</td>
</tr>
<tr>
<td>H100</td>
<td>0.20</td>
</tr>
<tr>
<td>H280</td>
<td>0.40</td>
</tr>
<tr>
<td>H350</td>
<td>0.60</td>
</tr>
</tbody>
</table>
Thermal Loading – TiO2

Temperature Rise Per Pass

Temperature Rise/ nm
Thermal Loading

**Cu**

- DC
- Pulsed DC
- H100
- H280
- H350

**TiO2**

- Pulsed DC
- 200A
- 400A
Discussion

➢ Copper
  ➢ Dynamic deposition rate decreases with pulsing and increase in pulsed peak power due to metal ion return to the target
  ➢ Resistivity was the lowest for pure DC sputtering, most likely due to larger grain size

➢ TiO2
  ➢ Dynamic deposition rate decreases with pulsing and increase in pulsed peak power due to metal ion return to the target
  ➢ Films cross-section shows film densification with HIPIIMS and increasing peak current and positive voltage reversal
  ➢ The index of refraction increases with HIPIIMS and increasing peak current and positive voltage reversal
Heat load

- The temperature rise per nm of deposited material increases with HIPIMS and increasing peak power and positive voltage reversal

Factors contributing to Heat load
- Heat of condensation
- Thermodynamic reactions at the surface
- Incoming energy of neutral species
- Incoming energy of gas and metal ions
- Electron heating
Conclusions

➢ HIPIIMS with Positive Voltage Reversal is useful for film densification and reduction in grain size

➢ The index of refraction and coating density of metal oxide coatings can be improved with HIPIIMS with Positive Voltage Reversal

➢ HIPIIMS with Positive Voltage Reversal can be integrated into existing R2R coaters
   ➢ It is a powerful tool for opening the process window as metal and gas ions can be energized from the sputtering target imparting greater energy to the growing film
   ➢ The tradeoff is slightly lower deposition rate and higher normalized thermal load
Future work

- Further examine higher peak current and positive voltage effects on grain size and electrical properties for Cu

- Look at resistivity of low mobility metal thin films with HIPIMS with positive voltage reversal

- Further analysis of optical properties of TiO₂ coatings and other metal oxides