

# HiPIMS: the advantages of a high ionization plasma PVD technology

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#### Dream Team



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# Why coatings?

There are ever increasing demands on

- ✓ performance,
- $\checkmark$  product quality, and
- ✓ development of new materials.

The ability to coat objects with a film allows
 combining the properties of the underlying material and the coating,

✓ increasing cost efficiency.

Existing products improvement
 New materials and properties







# Why sputtering?

- Wide range of possible sputtered materials including compounds an alloys
- $\checkmark$  High deposition rates
- High purity films (vacuum, low pressure)
- ✓ Good coating/substrate adhesion
- ✓ Good step coverage and uniformity
- ✓ Allow various parameter control
- ✓ Scalability ✓ .....







#### Thin film deposition by Sputtering

- ✓ Sputtering = ejection of atoms due to bombardment of the target by ions.
- ✓ The source of ions is a plasma discharge.
- ✓ Secondary electrons are also emitted.



#### **Magnetron Sputtering**

#### A sputtering device with an effective electrons trapping!



A. Anders, Surf. Coat. Technol. 205 (2011) S1. A. Anders, Journal of Applied Physics 121 (2017) 171101.

# Structure Zone Diagram

In MS techniques, variation of the deposition parameters allows for control of the **energy/momentum** transferred to the film-forming species enabling the manipulation of the **film properties**.



Thornton, J. Vac. Sci. Technol. 11 (1974) 666

# HiPIMS



< 10% duty cycle (on/off time ratio)

#### Typical Voltage/Current/Power signals



V. Kouznetsov, K. Maca'k, J. M. Schneider, U. Helmersson, and I. Petrov, Surf. Coat. Technol. 122 (1999) 290.
 A. Anders, Surface and Coatings Technology 205 (2011) S1-S9.



CrN Glancing Angle Deposition

Inclination of columns is reduced at high target current densities due to high ion-to-neutral ratio



G. Greczynski, et al., Thin Solid Films **519** (2011) 6354.

Cross-sectional SEM images of Ta films grown by (a) HiPIMS and (b) DCMS on a Si substrate clamped on the side of a trench.



- ✓ HiPIMS films → dense with columns growing perpendicular to the Ta/Si interface.
- ✓ DCMS films → porous microstructure with columns inclined toward the flux direction (atomic shadowing).

J. Alami et al., Journal of Vacuum Science and Technology A, 23 (2005) 278.

Cross sectional SEM images of TiAIN coating deposited on the flank and the rake side of a cutting insert.



K. Bobzin, N. Bagcivan, P. Immich, S. Bolz, J. Alami, R. Cremer, J. Mater. Process. Technol. 209 (2008) 165





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#### Phase composition tailoring



# Phase composition tailoring





(a) Parallel (b) Perpendicular

- Light elements like C are 0 favored at the expense of heavier elements (Ti and Si) along the target normal!
- Substrates placed at an angle 0 of 90° with respect to the target experience a < flux of C because of the < ionization degree of C compared to Ti and Si

D. Lundin, and K. Sarakinos, Journal of Materials Research 27 (2012) 780.

# Phase composition tailoring

 $\gamma$ -Mo<sub>2</sub>N  $\rightarrow$  fcc phase (Fm3m)  $\delta$ -MoN  $\rightarrow$  hexagonal phase (P6<sub>3</sub>mc)



 $\delta$ -MoN exhibits a low compressibility,

> H and E, < COF and > wear resistance.





At T<<300°C Mo-N with a high % of  $\delta$  phase

Sample	Phase	a (Å)	c (Å)	Concentration (% <sub>wt</sub> )	(C <sub>γ</sub> /C <sub>δ</sub> ) <sub>%wt</sub>
T1	γ-Mo <sub>2</sub> N	4.2196	-	23.8	0.31
	δ-MoN	5.8372		76.2	
T2	γ-Mo <sub>2</sub> N	4.1751	-	26.8	0.37
	δ-MoN	5.8103	5.621	73.2	
Reference	γ-Mo <sub>2</sub> N	4.1616			
Bulk	δ-MoN	5.7395	5.6176		

#### Rietveld method:

 $\circ$  a, c  $\rightarrow$  cell parameters;

(C<sub>γ</sub>/C<sub>δ</sub>)<sub>%wt</sub> → wt.
 concentration ratio between γ and δ phases.

V. Zin, E. Miorin, F. Montagner, M. Fabrizio, S. M. Deambrosis, Tribology International 119 (2018) 372-380.



TiB<sub>2</sub> SEM Analysis: morphology and microstrucure



#### TiB<sub>2</sub> Mechanical Properties: H and E



**Elastic Modulus** 



#### TaAIN 50%

#### TaAIN 5%



#### Ball-on-flat wear test

- 5 mm Al<sub>2</sub>O<sub>3</sub> ball (H=16.7, E=365 GPa)
- Sliding speed: 10 mm/s
- Normal load: 3 N
- Track I: 3mm







# Interface engineering

Highly ionized fluxes + substrate bias = ion energies 100s ÷ 1000s eV

#### Film-substrate interface engineering to

- ✓ affect the growing mode
- $\checkmark$  enhance adhesion



S.M. Deambrosis, et al. Surface and Coatings Technology, 354 (2018) 56-65.



Power (W)	500
Voltage (V)	900
Frequency (Hz)	500
Pulse † (µsec)	25
Bias V (V)	1000
Initial T (°C)	RT
Final T (°C)	200





# Interface engineering



#### Insulating substrates

#### Metallic membranes for hydrogen separation



SEM BS electron image of  $PdAg/Al_2O_3$  membrane (8.7 µm).

SEM BS electron image of a  $Pd/V_{93}Pd_7/Pd/Al_2O_3$  membrane (4.2  $\mu$ m).

S. Fasolin, S. Barison, S. Boldrini, A. Ferrario, M. Romano, F. Montagner, E. Miorin, M. Fabrizio, L. Armelao, International Journal of Hydrogen Energy 43 (2018) 3235 - 3243; doi.org/10.1016/j.ijhydene.2017.12.148.
S. Barison, S. Fasolin, S. Boldrini, A. Ferrario, M. Romano, F. Montagner, S.M. Deambrosis, M. Fabrizio, L. Armelao, International Journal of Hydrogen Energy 43 (2018) 7982 - 7989; doi.org/10.1016/j.ijhydene.2018.03.065.

#### Insulating substrates

#### Nitride membranes for hydrogen separation



a-Al<sub>2</sub>O<sub>3</sub> discs  $\Phi$  = 15mm, 25mm Thickness = 2mm Porosity1 = 80nm Porosity2 = 3-5nm (lapped on one side +  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> film).



#### **HiPIMS** deposition rate



M. Samuelsson, D. Lundin, J. Jensen, M. A. Raadu, J. T. Gudmundsson, and U. Helmersson, Surface and Coatings Technology, 202 (2010) 591.

#### https://hipims.cemecon.de/en/





# Grazie per l'attenzione!

#### Schematic of the Sputtering process



✓ A. Anders, Journal of Applied Physics 121 (2017) 171101.

J. F. Ziegler, J. P. Biersack, and U. Littmark, The Stopping and Range of Ions in Solids (Pergamon Press, New York, 1985).
 J. F. Ziegler and J. Biersack, see <a href="http://srim.org/see">http://srim.org/see</a> "Monte Carlo code SRIM2013, 2013.

- ✓ Sputtering is the ejection of atoms due to bombardment of a solid surface (the target) by energetic particles (often ions).
- ✓ The source of ions for the sputtering process is achieved by a plasma discharge.
- ✓ Secondary electrons are also emitted from the target surface as a result of the ion bombardment.

#### Unbalanced magnetrons

A first step to using the plasma of the magnetron to assist film growth



 Plasma escapes from target region, providing assistance to film growth.

 $n_e \sim 10^{12}$  cm<sup>-3</sup>, up to a distance of 10 cm.

**NbN** 



B. Window and N. Savvides, J. Vac. Sci. Technol. A 4, 196 (1986). J.J. Olaya, et al., Thin Solid Films 516, Issue 23 (2008) 8319-8326.

#### A Generalized Structure Zone Diagram including the Effects of Plasma Assistance to Film Growth



A. Anders, Thin Solid Films 518 (2010) 4087

# **HiPIMS** Advantages

High pulsed ion fluxes are available at the substrate and affect the film growing and properties.

#### derived from Thornton's diagram .....



Deposition on
 Complex-Shaped
 substrates

- > Phase composition tailoring by HiPIMS
- Control of film

microstructure

> Interface engineering

A. Anders, Thin Solid Films 518 (2010) 4087

# CNR-ICMATE PVD lab

# Coating Deposition Lab.

In our laboratories the equipments for the PVD deposition (Physical Vapor Deposition) by Magnetron Sputtering of thin films consists of three completely independent systems:

- 1. Confocal chamber, for the deposition of multi-component films via co-sputtering.
- 2. Multi-layer chamber, for the deposition of multilayer films.
- 3. HiPIMS (High Impulse Magnetron Sputtering) chamber.

#### **HiPIMS** Chamber



# **HiPIMS** Chamber



- > Multi-magnetron equipment
- Substrate rotation and vertical positioning
- > Working up to  $500^{\circ}C$ ,
- > Bias voltage up to 1.2 kV for substrate etching
- > I-V Probes
- > Optical Spectroscopy
- Microbalance with quartz crystals
- Process control interface









# **Confocal and Multilayer Chambers**



#### Confocal and Multilayer Chambers: Cathode layout

#### **Confocal Chamber**



#### Multilayer Chamber



# **HiPIMS Chamber Power Supply**



# 2<sup>nd</sup> HiPIMS Power Supply



#### Other PVD Power Supply: DC, Pulsed DC, RF









Especially designed to used to prevent the formation of arcs. Reactive sputtering processes of difficult materials.



It is possible to sputter insulating target because no current could flow through the insulator

# **Characterization facilities**

- Morphological
- Chemical
- Structural
- Mechanical
- Tribological
- Thickness

UMT - Tester



#### Nanoindenter



SEM / EDS



**Mechanical Profiler** 







XRD



Calotest



# Applications of the HiPIMS technique

- ✓ Hard coatings
- ✓ Adhesion enhancement
- Corrosion protection layers
- ✓ Optimized Tribological performance
- ✓ Optical coatings
- ✓ Electrical coatings

 $\checkmark$ 

HiPIMS TiAlN coatings: film/substrate interface design effect on high temperature cyclic oxidation behavior





#### General Electric GEnx Jet Engine:

 $\gamma$ -TiAl for Low Pressure Turbine blades and High Pressure Compressor blades to increase the thrust-toweight ratio.





- S.M. Deambrosis, F. Montagner, V. Zin, M. Fabrizio, C. Badini, E. Padovano, M. Sebastiani, E. Bemporad, K. Brunelli, E. Miorin, "Ti1-xAlxN coatings by Reactive High Power Impulse Magnetron Sputtering: film/substrate interface effect on residual stress and high temperature oxidation", Surface and Coatings Technology, 354 (2018) 56-65; https://doi.org/10.1016/j.surfcoat.2018.09.004.
- C. Badini, S.M. Deambrosis, E. Padovano, M. Fabrizio, O. Ostrovskaya, E. Miorin, G. D'Amico, F. Montagner, S. Biamino, V. Zin, "Thermal Shock and Oxidation Behavior of HiPIMS TIAIN Coatings Grown on Ti-48AI-2Cr-2Nb Intermetallic Alloy", Materials 9 (12) (2016) 961; doi: 10.3390/ma9120961.
- C. Badini, S.M. Deambrosis, O. Ostrovskaya, V. Zin, E. Padovano, E. Miorin, M. Castellino, and S. Biamino. 2017. "Cyclic Oxidation in Burner Rig of TiAlN Coating Deposited on Ti-48Al-2Cr-2Nb by Reactive HiPIMS", Ceramics International, 43, 7 (2017) 5417-5426; https://doi.org/10.1016/j.ceramint.2017.01.031.

Mechanical and tribological properties of Mo-N coatings deposited via HiPIMS on temperature sensitive substrates









V. Zin, E. Miorin, F. Montagner, M. Fabrizio, S. M. Deambrosis, "Mechanical properties and tribological behaviour of Mo-N coatings deposited via high power impulse magnetron sputtering on temperature sensitive substrates", Tribology International 119 (2018) 372-380; https://doi.org/10.1016/j.triboint.2017.11.007.



E. Miorin, F. Montagner, V. Zin, D. Giuranno, E. Ricci, M. Pedroni, V. Spampinato, E. Vassallo, S.M. Deambrosis, "Aluminum rich PVD coatings to prevent T91 steel corrosion in stagnant liquid lead: promising results" SUBMITTED to Surface and Coatings Technology.



- S. Fasolin, S. Barison, S. Boldrini, A. Ferrario, M. Romano, F. Montagner, E. Miorin, M. Fabrizio, L. Armelao, International Journal of Hydrogen Energy 43 (2018) 3235 – 3243; doi.org/10.1016/j.ijhydene.2017.12.148.
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# Deposition on complex-shaped substrates

Cross-section SEM image of two via holes with an aspect ratio 1:2 homogeneously filled by Cu using HiPIMS.



V. Kouznetsov, K. Macak, J.M. Schneider, U. Helmersson, I. Petrov, Surf. Coat. Technol. 122 (1999) 290



XRD patterns of Ta films deposited by HiPIMS on Si substrates, biased at negative potentials up to 90 V. The bcc  $\alpha$ -Ta phase is obtained at 70 V.



HiPIMS process ionbombardment influences the internal stresses of the growing films and allows depositing  $\alpha$ -Ta at room T!

J. Alami et al., Thin Solid Films, 515 (2007) 3434.



XRD patterns of  $TiO_2$  films grown on Si substrates by HiPIMS at various values of peak target power.

 $\checkmark$  The rutile phase can be achieved even at room T!

 $\checkmark$  > peak target power = > number of ions available during deposition  $\rightarrow$  formation of the rutile at the expense of the anatase phase!

M. Aiempanakit et al., Surface and Coatings Technology, 205 (2011) 4828.

γ-Mo<sub>2</sub>N → face-centered cubic (space group Fm3m) δ-MoN → hexagonal phase (space group P6<sub>3</sub>mc)



δ-MoN phase exhibits a low compressibility, > H and E,
< COF and > wear resistance.



- Even at T<<300°C, HiPIMS technology allows obtaining Mo-N with a >% of  $\delta$  phase.
- Even at T<<300°C, it was possible to deposit suitable coatings for tribological purposes.

Sample	Phase	a (Å)	c (Å)	Concentration (% <sub>wt</sub> )	(C <sub>γ</sub> /C <sub>δ</sub> ) <sub>%wt</sub>	
T1	γ-Mo <sub>2</sub> N	4.2196	-	23.8	0.21	
	δ-ΜοΝ	5.8372		76.2	0.31	
T2	γ-Mo <sub>2</sub> N	4.1751	-	26.8	0.37	
	δ-ΜοΝ	5.8103	5.621	73.2		
Reference Bulk	γ-Mo <sub>2</sub> N	4.1616				
	δ-ΜοΝ	5.7395	5.6176			

#### Rietveld method:

- a, c  $\rightarrow$  cell parameters;
- (C<sub>γ</sub>/C<sub>δ</sub>)<sub>%wt</sub> → wt.
   concentration ratio between γ and δ phases.

Measured H values were comparable, or even superior, to literature hardness data

Technique	Т (°С)	δ-ΜοΝ	γ- <b>Mo</b> ₂N	H (GPa)	Thickness (μm)
HiPIMS	<160	yes	yes	22-28	8
arc-PVD	300	yes	yes	20	2
arc-PVD	450-500	yes	yes	32-38	1.5-2.3
arc-PVD	>400	yes	yes	47	1.1-3.5
RF-MS	300	no	yes	23	1.5
RF-MS	230	yes	yes	20-23	1-2
pulsed DC-MS	350	no	yes	24.5	2



Yttria-Stabilized Zirconia (YSZ) thin films are reactively sputterdeposited by high power impulse magnetron sputtering (HiPIMS) in an industrial setup on porous NiO/YSZ fuel cell anodes.



SEM micrographs of films deposited at bias voltages –180 V (a, c) and –120 V (b). The peak power density was 0.6 kW cm<sup>-2</sup> and the deposition pressure ~750 mPa.

S. Sønderby et al. / Surface & Coatings Technology 281 (2015) 150-156

#### AlTiN via DCMS

#### Altin via Hipims



#### TaAIN via DC-MS

#### TaAIN via HiPIMS



#### VN



#### SEM analysis: Microstructure

# <section-header>

#### HiPIMS



#### TiB<sub>2</sub> SEM Analysis: Microstructure







# Interface engineering

#### **HiPIMS Metal Etching Pre-treatment**



Presence of an unwanted droplet **in arc Cr etching** [C. Schonjahn, L. A. Donohue, D. B. Lewis, W.-D. Munz, R. D. Twesten, and I. Petrov, J. Vac. Sci. Technol. A 18, 4 (2000)].



CrAlN layer grown on the  $\gamma$ -TiAl substrate after **HiPIMS Cr pretreatment**. Uniform diffraction contrast is shown [A. P. Ehiasarian, J. G. Wen and I. Petrov. Journal of Applied Physics 101, 054301(2007)].

Wear mechanism of single and multilayer coatings









