UMONS
Université de Mons

High-Power Impulse Magnetron Sputtering

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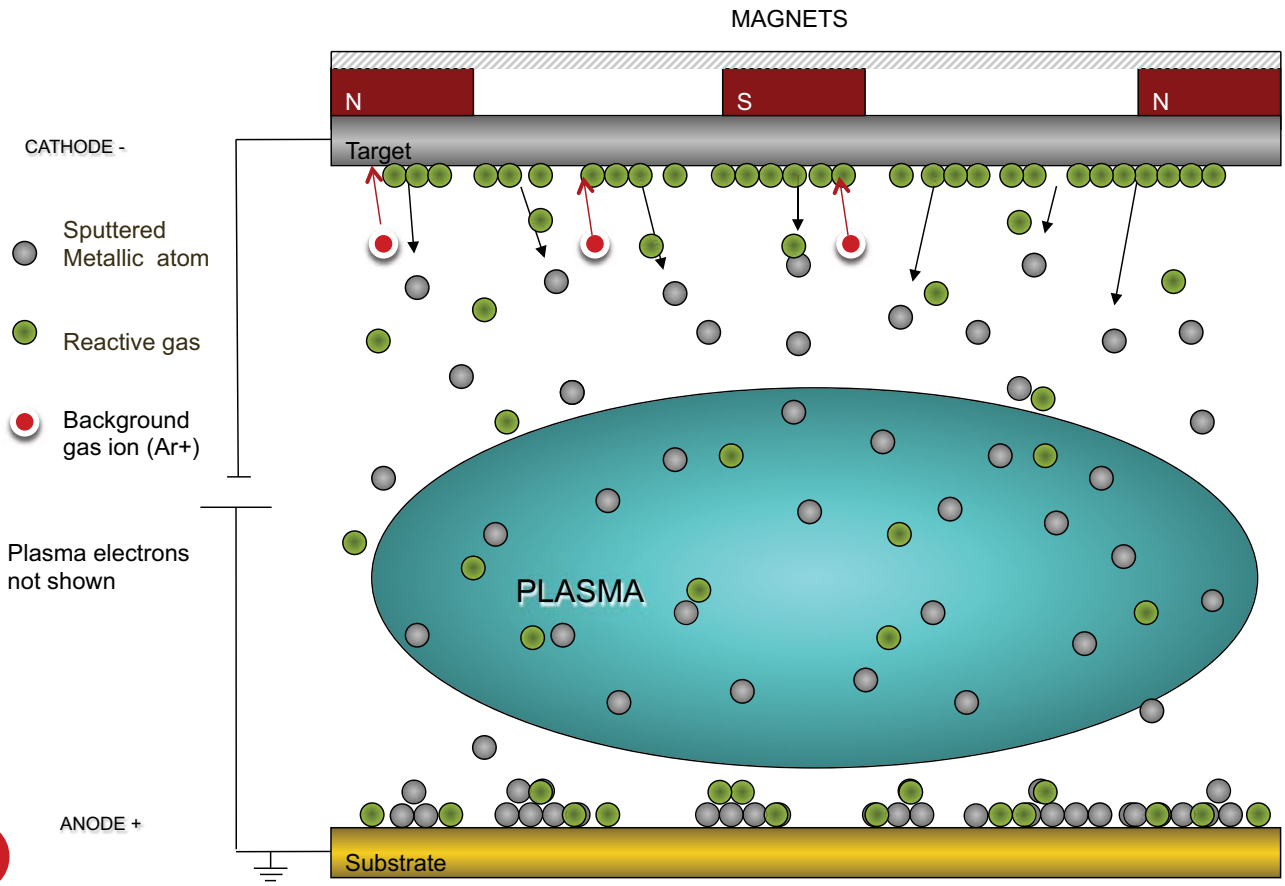
CHIPS
Chimie des Interactions Plasma Surfaces

Outline

- Why HiPIMS ?
- How to generate HiPIMS plasmas ?
- What can we get with such a plasma ?
  - Plasma physics and plasma-surface interactions
  - Thin film properties
- Concluding remarks

Principle of reactive magnetron sputtering

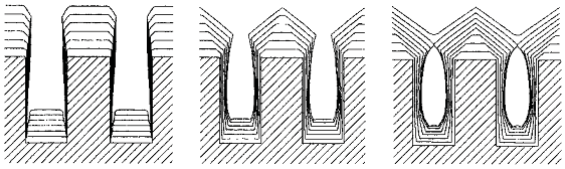


Why HiPIMS ?

Sputtered vapor is made of neutral atoms/clusters

No conformal coverage

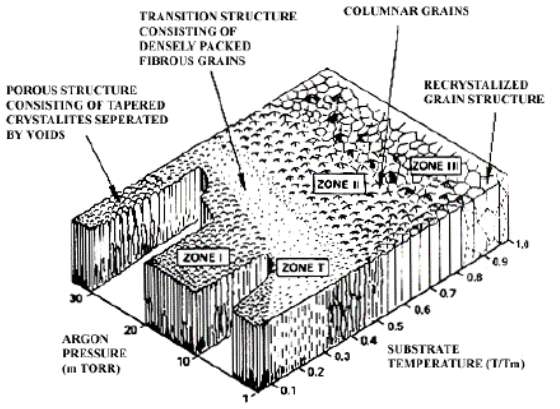
DC magnetron, Cu^0



S. Hamaguchi and S. M. Rossnagel,
J. Vac. Sci. Technol. A 14 (1996).

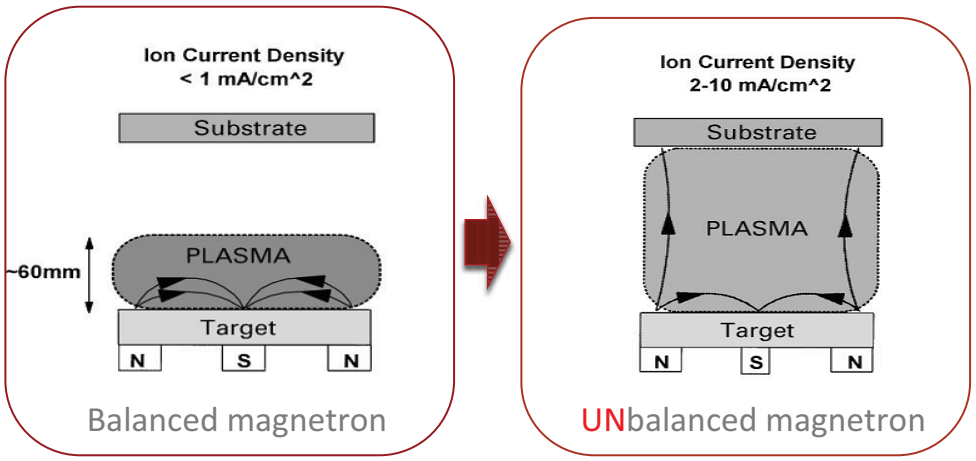
Control of the film microstructure through

- Substrate heating
- Varying working pressure



J.A. Thornton, J. Vac. Sci. Technol. A 4/6 (1986).

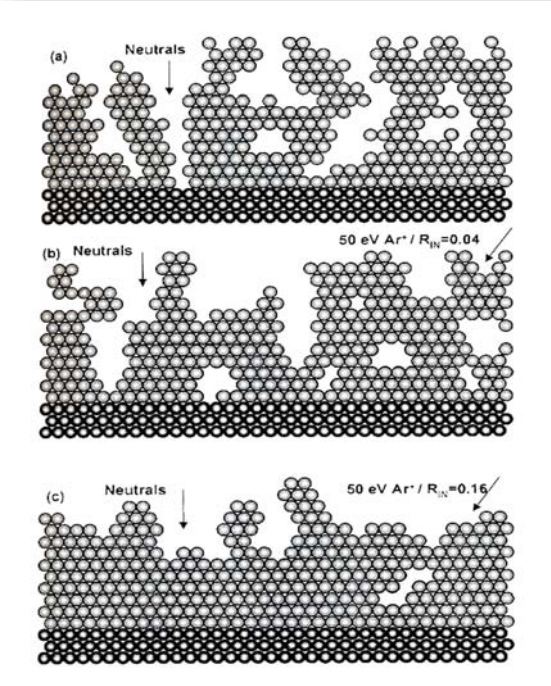
Ion bombardment assisted film growth



Ion bombardment by Ar^+ ions

Kelly & Arnell, Vacuum 56 (2000)
B. Window, JVST A. 4, 453 (1986).
B. Window, JVST A, Film. 4, 196 (1986).

Film densification by ion bombardment



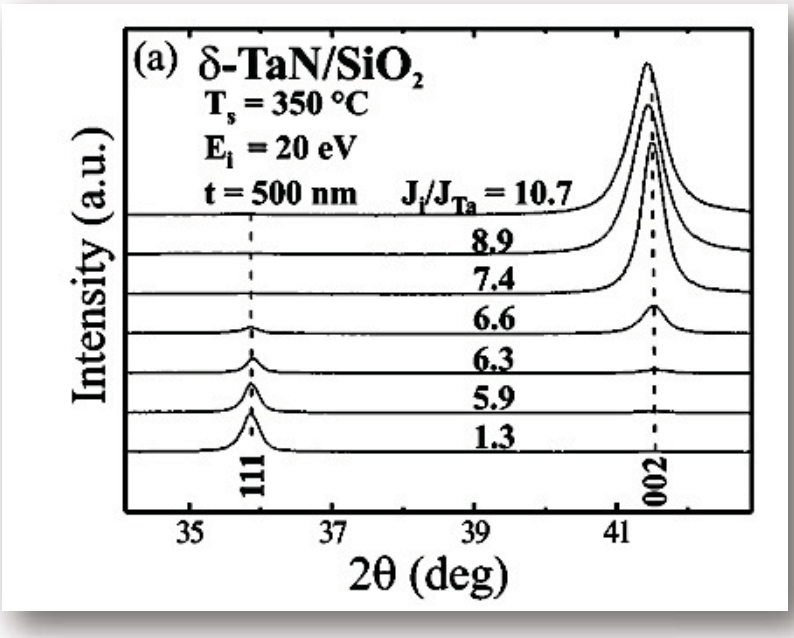
Deposition with neutrals only

Neutrals +
50 eV Ar+ (4%)

Neutrals +
50 eV Ar+ (16%)

A. Anders, *Handbook of plasma immersion ion implantation and deposition*, Wiley, 2000.

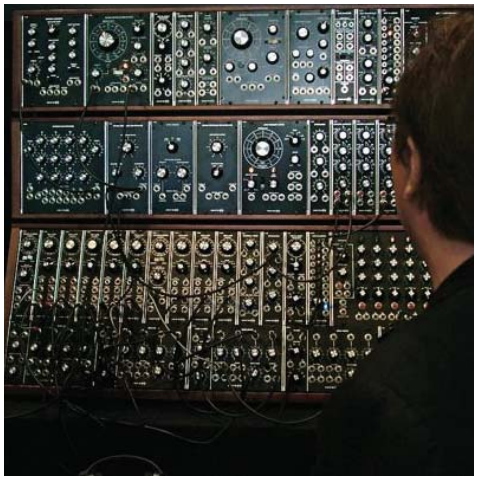
Evolution of texture with the ion bombardment



J_i/J_{Ta}

Chun *et al* J. Appl. Phys. (1999).

Energetic particle bombardment provides more knobs to « tailor » films properties.



But

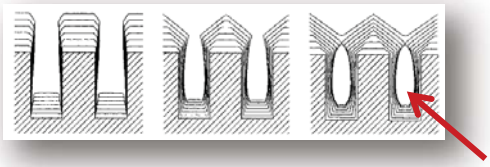
- Ar^+ bombardment may results in Ar incorporation in the film [1]
- which can induce :
  - Increase of film internal stress [2]
    which can be detrimental to mechanical properties
  - Decrease of electric conductivity [3]
  - Modification of the film microstructure [4]
  - …

[1] Windischmann, Critic. Rev. Solid State Mater. Sci. (1992)
[2] Mounier & Pauleau, Diam. Relat. Mater. (1997)
[3] Catania *et al*, J. Appl. Phys (1993)
[4] Houska *et al*, J. Phys.C :Condes. Matter (2006)

The solution…

- Is to Ionize the *sputtered metal atoms*
  - Controlling kinetic energy of the film forming species
    - Energetic particle (Ion) bombardment during growth
  - Controlling the trajectory of the film forming species
    - allowing conformal deposition with biased substrate

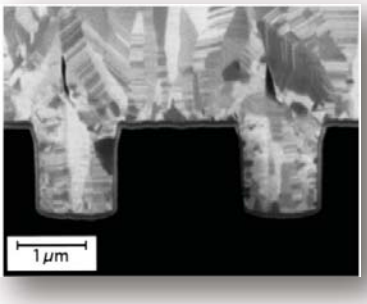
DC magnetron, Cu^0



void

Hamaguchi *et al, JVSTA (*1996)

HiPIMS, Cu^+



Kouznetsov *et al* Surf. Coat. Technol. (1999)

Ionized Physical Vapor Deposition & Ionized magnetron discharges

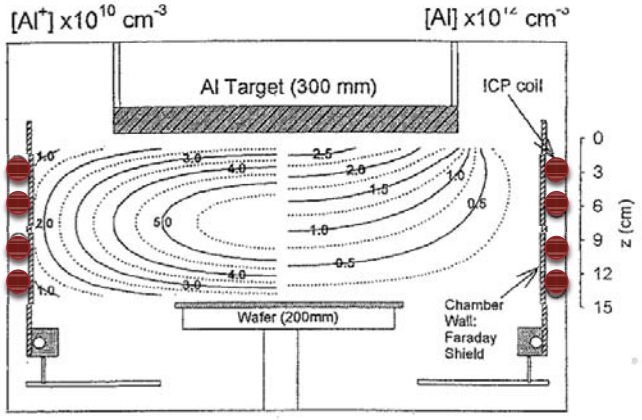
The basic idea :

➔ Increase the ionization rate of the sputtered metal atoms by enhancing the electron impact probability

- Need more hot electrons in the plasma bulk
- Necessary to enhance electron - electric field interaction

A new deposition technique has been developed which combines conventional magnetron sputter deposition with a rf inductively coupled plasma(RFI). The RFIplasma is located in the region between the magnetron cathode and the sample position, and is set up by a metal coil immersed in the plasma. A large fraction of the metal atoms sputtered from the magnetron cathode are ionized in the RFIplasma. By placing a negative bias on the sample, metal ions are then accelerated across the sample sheath and deposited at normal incidence. Results from a gridded energy analyzer configured with a microbalance collector and located at the sample position indicate the level of ionization is low at a few mTorr and rises to ≥80% at pressures in the 25–35 mTorr range. Optical measurements of metal ion and neutral emission lines show scaling of the relative ionization to higher discharge powers. Significant cooling of the plasma electron temperature is observed when high concentrations of metal atoms were sputtered into the plasma.

S.M. Rossnagel and J. Hopwood, Appl. Phys. Lett. 63, 3285 (1993).



Dickson et al J. Vac. Sci. Technol. B 16, 523–531 (1998).

The working principle of HiPIMS glow discharges

In order to increase the ionization rate of the sputtered material at conventional working pressures

- Increase the target voltage (as compared to DCMS)
- To increase electron density (inside the magnetized plasma) and target current
  - In magnetron discharge : $I = kV^n$

But

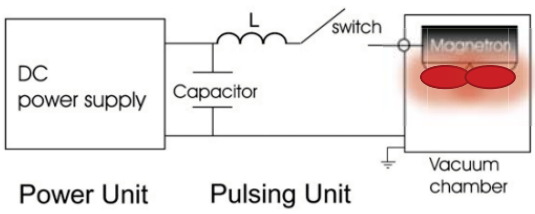
- the time-averaged power must be kept to conventional DCMS level

in order to avoid overheating the magnets

⇨ High-Power Pulses at the magnetron target with low duty cycle (<1%)

Sarakinos, Alami, Konstantinidis, Surf. Coat. Technol. (2010)

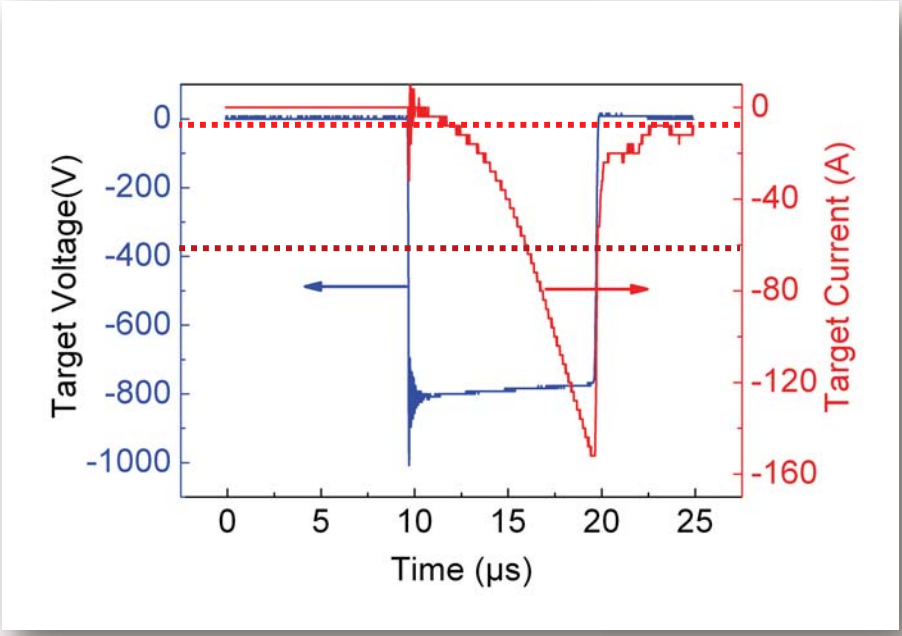
Basic architecture of an HiPIMS power supply



1. The dc generator charges the capacitor bank of a pulsing unit.

2. The energy stored in the capacitor is dissipated into the plasma in pulses of well-defined width and frequency using fast switches.

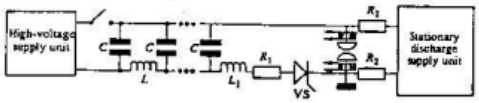
Typical I – V waveforms



Typical peak currents and power densities = ~A/cm² and ~kW/cm²

Earlier studies

Mozgrin et al studied the feasability of high-current low-pressure
quasi stationary discharge in E x B fields [1]



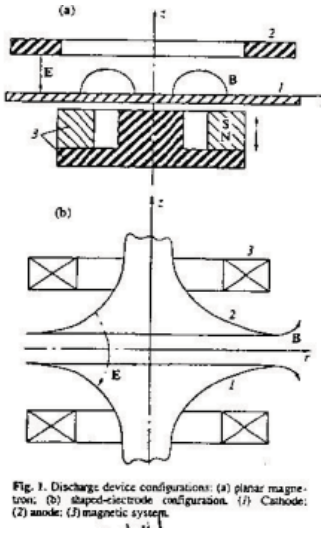


Fig. 1. Discharge device configurations: (a) planar magnetron; (b) shaped-electrode configuration. (1) Cathode; (2) anode; (3) magnetic system.

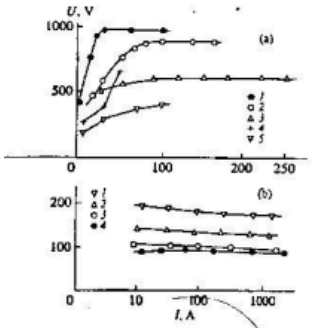


Fig. 5. (a) High-current magnetron discharge: (1) planar magnetron, Cu, $p = 5 \times 10^{-3}$ torr, Ar; (2) planar magnetron, Ti, $p = 5 \times 10^{-3}$ torr, Ar : N_2 = 4 : 1; (3) planar magnetron, Ti, $p = 10^{-2}$ torr, N_2; (4 and 5) shaped-electrode system, Cu, $p = 5 \times 10^{-2}$ torr, He : H_2 = 1 : 1, and Cu, $p = 10^{-1}$ torr, Ar. (b) High-current diffuse regime: (1 and 2) shaped-electrode system, Cu, p = 1 torr, He : H_2 = 1 : 1 and Cu, $p = 10^{-1}$ torr, He : H_2 = 1 : 1; (3) planar magnetron, Cu, $p = 10^{-1}$ torr, Ar; (4) planar magnetron, Cu, $p = 10^{-1}$ torr, Ar : SF_6 = 4 : 1.

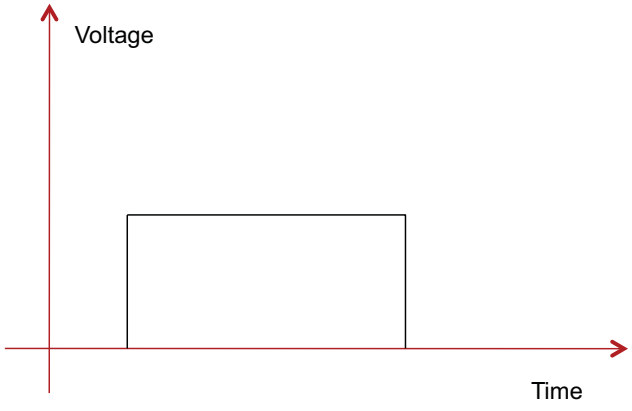
[1] Mozgrin et al, Plasma Phys. Rep. 1995.

Several approaches to generate HiPIMS discharges

- HiPIMS « categories » : short, regular, large,and X-Large pulses
- Variations and added features

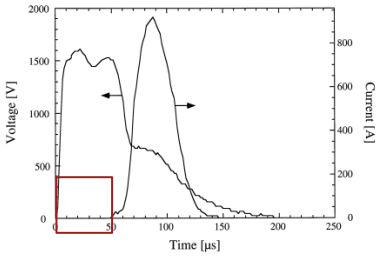
Several approaches to generate HiPIMS discharges

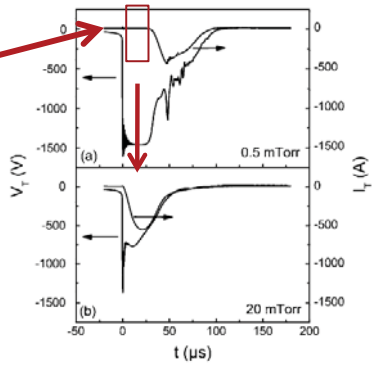
- Approaches can be « differentiated » by the pulse duration
  1. Regular (50 – 200µs) (« First » HiPIMS)
  2. Short (1 – 20µs)
  3. Large (200 – 400µs)
  4. X-Large (400 – 4000µs)



Regular Pulses (50 – 200µs)

- Seminal paper from Kouznetsov *et al* [1]
  - 50µs time dead time before current starts flowing
  - Discharge breakdown through ionizing collision cascade needs time to proceed
  - Influence of pressure, frequency, pulse peak current [2,3]

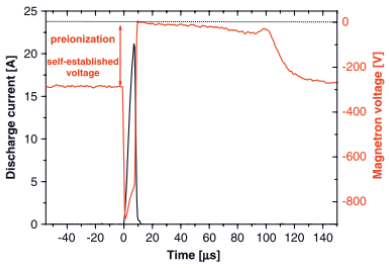




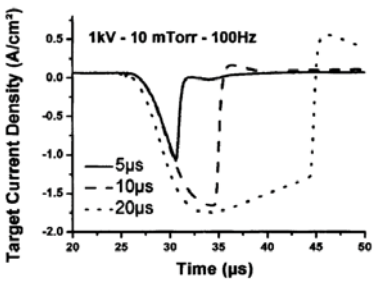
[1] Kouznetsov *et al*, Surf. Coat. Technol. 1999
[2] Konstantinidis, Thesis, 2004
[3] Alami *et al*, Plasma Sources Sci. Technol. 2005

Short pulses (1 – 20µs)

- Technology based on plasma preionization [1]
- Facilitate the discharge generation
  - Preionization = electron ready to respond to fast increase of cathode voltage
    - Preionization can be achieved by
      - DC voltage (few mA is enough)
      - RF or µW secondary plasmas
      - High repetition frequency (>500Hz)
- Fast current rise is guaranteed ⇒ short high-power pulses
- Short pulses allow arc-free process even during reactive mode [2]



Vasina *et al*, Plasma Sources Sci. Technol. 2007.

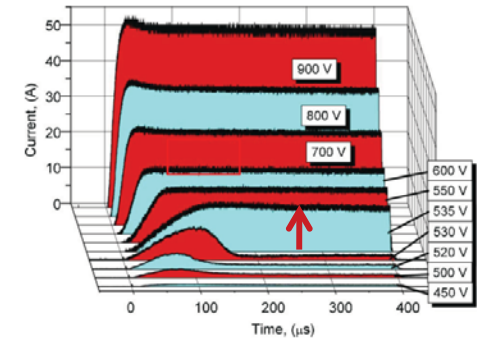


Konstantinidis *et al,* J. Appl. Phys. 2006

[1] Ganciu, Konstantinidis *et al*, J. Opt. Adv. Mat. 2005.
[2] Konstantinidis *et al* Thin Solid Films, 2006

Large pulses (200 – 400μs)

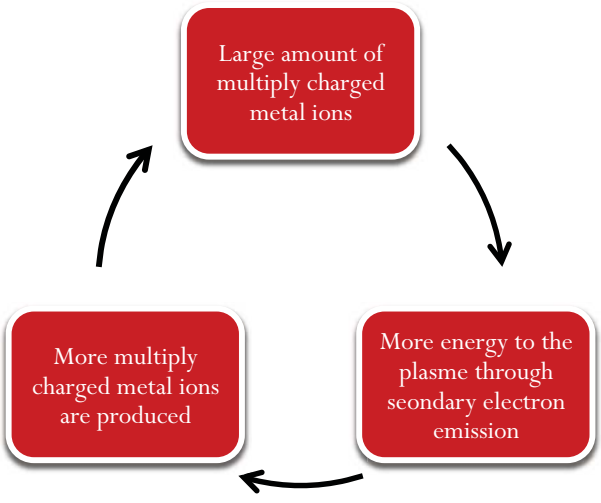
- High peak power density ($\geq 5 kW/cm^2$), 2 inch target
- Self-sputtering runnaway is achieved at a precise voltage (535 V for Cu)



Anders, Andersson, Ehiasarian, J. Appl. Phys. 2007

Self-sputtering runnaway during HiPIMS

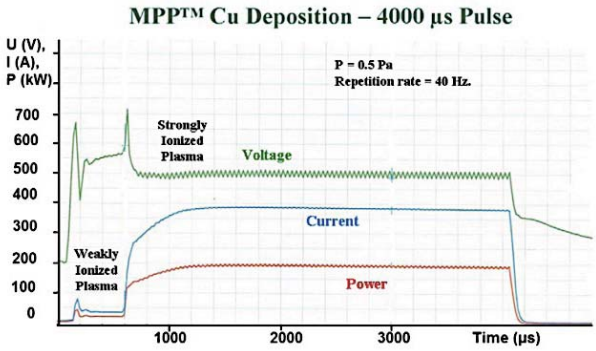
- Self-sustained self-sputtering can be ignited if $\alpha\beta\gamma_{ss} > 1$
  - α is the probability for a sputtered atom to become ionized,
  - β is the probability for the ion to return to the target
  - γ_{ss} is the yield of self-sputtering
    - High power + long pulses to achieve this state
    - If power is high ⇒ acceleration of this process (runnaway)
- Multiply charged metal ions are important actors in the process
  - Enhance the emission of secondary electrons (Kinetic emission)



Anders, Appl. Phys. Lett. 2008

X-Large pulses (400 – 4000µs)

- Several « stages » during main pulse (modulated pulse power) allow stable discharge
  - Low ionization step
  - High ionization step
- Deposition rates higher than DC were reported for reactive sputtering [1]

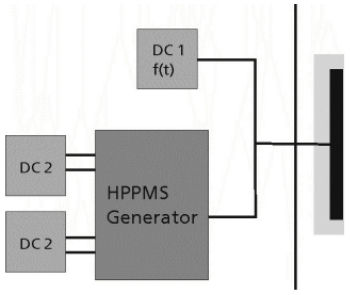


Chistyakov et al, SVC 2007.

[1] Chistyakov, Abraham, Sproul, SVC 2006.

Variations of HiPIMS:
1. HiPIMS with Superimposed DC

- Superimposed DC magnetron plasma to the HiPIMS discharge
- To increase deposition rate



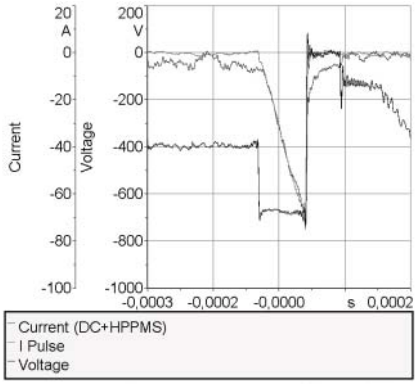


Figure 4: HPPMS for titanium sputtering; t_{on}: 90µs, t_{off}: 2190µs, U_{HPPMS}: 680V, 1kW supplying the pulse unit, 1.0kW dc power superimposed, UDC: 390V.

Bandorf, Falkenau, Schmidt, Mark, SVC 2007.

Variations of HiPIMS:
2. HiPIMS with Superimposed MF

- Superimposed MF magnetron plasma to the HiPIMS discharge
- To increase deposition rate
- Increase process stability in reactive mode

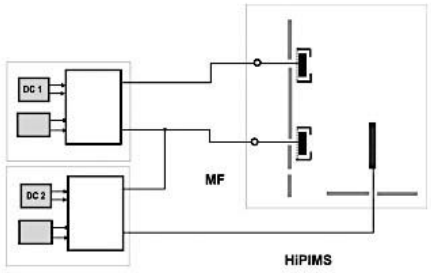


Figure 3: Setup for the superimposed MF + HiPMIS pulse pattern. The bottom generator is used for the HiPIMS pulses while the top generator is used for the MF pulses.

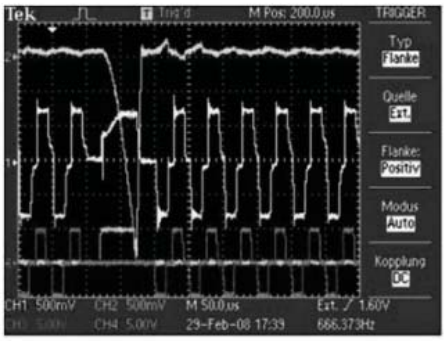
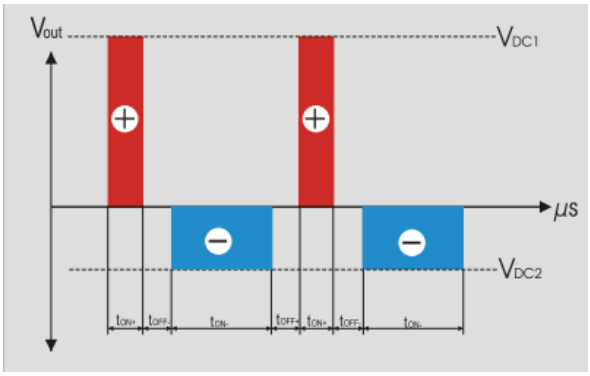


Figure 5: Screenshot of the pulse forms. Top: target current 300A; mid: target voltage 375V; bottom: control pulses. The length and the frequency of the HiPIMS pulse was 50µsec and 666Hz, respectively, the MF-frequency was 20.0 kHz.

Vergöhl, Werner, Bruns, Wallendorf, Mark, SVC 2008.

Variations of HiPIMS:
3. Bipolar HiPIMS

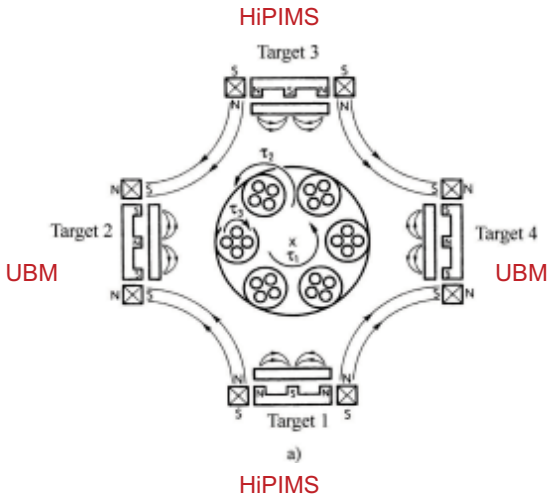
- Avoiding arcing during deposition of insulating films



http://www.melec.de/Brochure/BrochureSPIK1000A.pdf

Variations of HiPIMS:
4. Multicathode process

- Cathodes equipped with
  - Either DC
  - Or HiPIMS
  - High quality multilayered coatings + overcome deposition rate drawback



Purandare, Ehiasarian, Hovsepian, J. Vac. Sci. Technol. A 2008.

Added features :
Arc Handling for HiPIMS

- Arcing may occur
- Handling sequence :
  1. Arc is detected by some means (fast current rise).
  2. The source of power is disconnected from the arc at the load.
  3. Ehe energy stored in the pulse forming network inductor is moved elsewhere.
  4. In the best case, energy remaining in the discharge circuit is recycled to the main energy storage elements

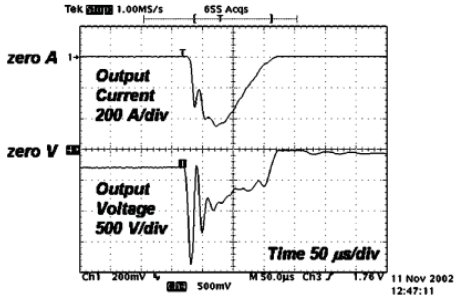


FIG. 5. Oscilloscope photo of normal operation into small magnetron.

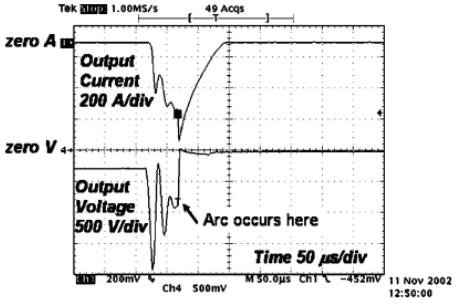


FIG. 6. Oscilloscope photo of arc handling into small magnetron.

Christie, Tomasel, Sproul, Carter, J. Vac. Sci. Technol. 2004.

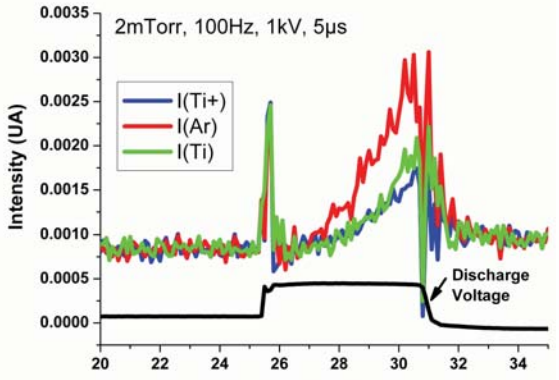
What can we get from such plasmas ?

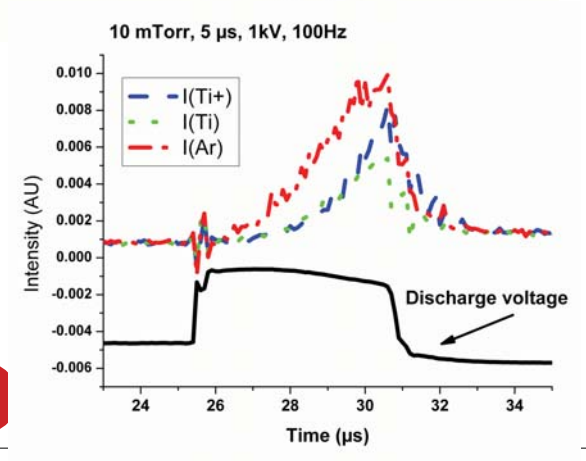
- Plasma physics and plasma-surface dynamics
- Thin film properties

What happens inside the plasma and at the target surface?

Ionization and deposition rate
Influence of the pulse ON time and pressure

Ti sputtered in Ar, target voltage = 1kV

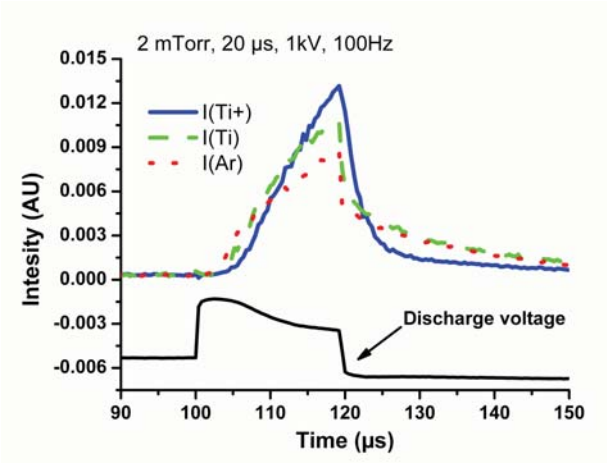


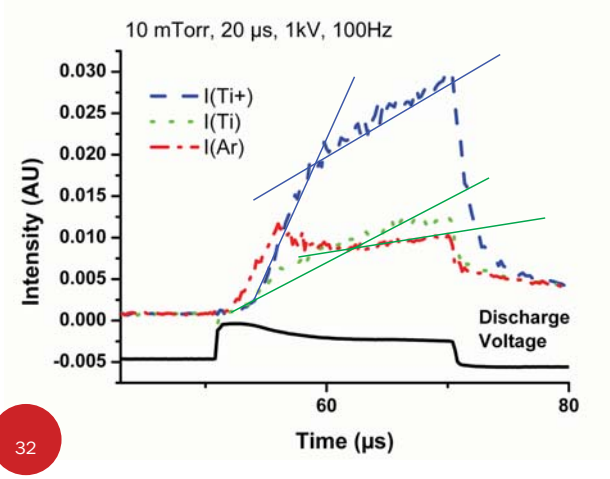


5µs – 2 and 10 mTorr

- Ar line first to rise
- Ar line dominates till the pulse ends
- At higher pressure

  I (Ti+) / I (Ti) ↑





20 µs – 2 and 10 mTorr

- Ti^+ line dominates
- At higher pressure
- Ti^+ / Ti ↑

➔ Metal ions are produced during the ON time.

➔ Ioniz. rates up to 90% + production of multiply charged metal ions

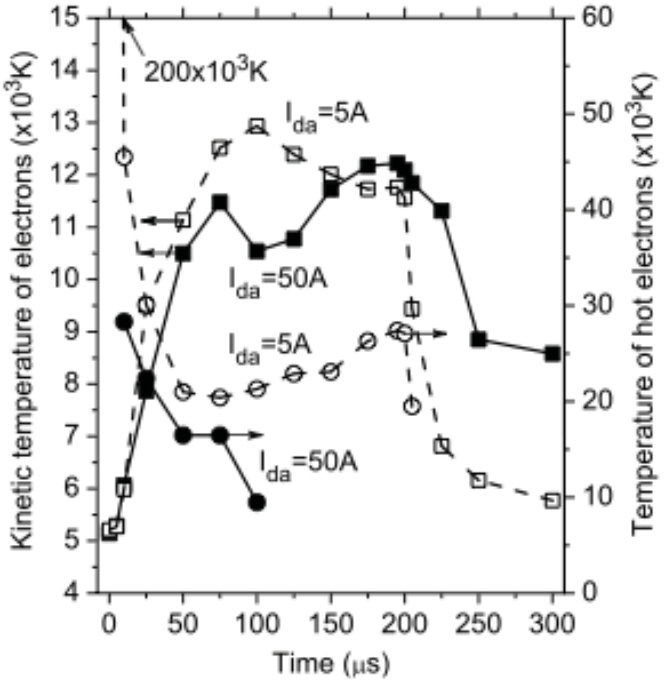
Let's note that

- I(Ar) stays constant
- I(Ti) and I(Ti^+) slopes decrease

➔ Why ?

- Is there less Ti atoms in the discharge ?
- The electron temperature decreases ?

Electron temperature during pulse ON time



D. Pajdarová et al, Plasma Sources Sci. Technol. 18, 025008 (2009).

Ionization mechanism

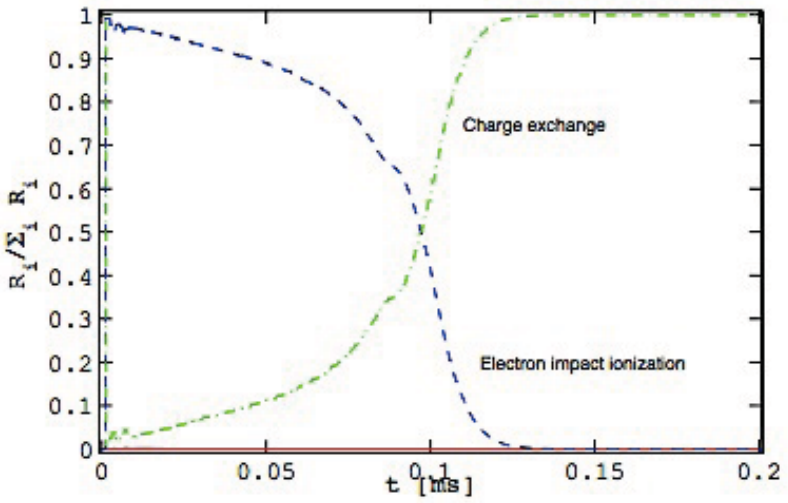
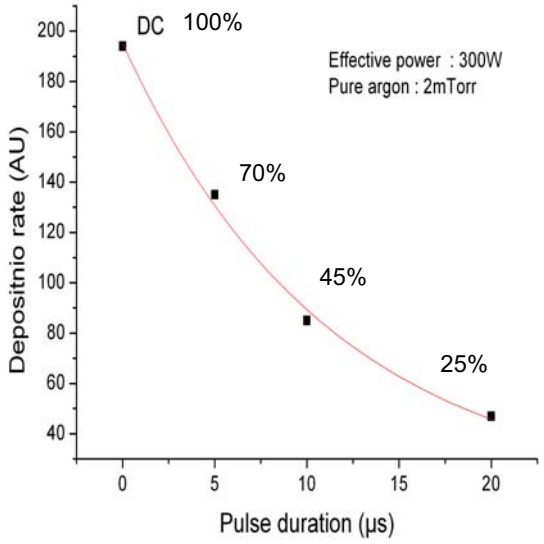


Figure 4. The relative reaction rate for the creation of the metal ion versus time from the pulse initiation.

Gudmundsson, J. Phys. Conf. Ser. 100, 082013 (2008).

Deposition rate is a function of pulse duration/ energy

Deposition rate decreases as the ionization increases



S. Konstantinidis et al, J. Appl. Phys. 99, 013307 (2006).

The decrease of the deposition rate : the major drawback of HiPIMS technology…

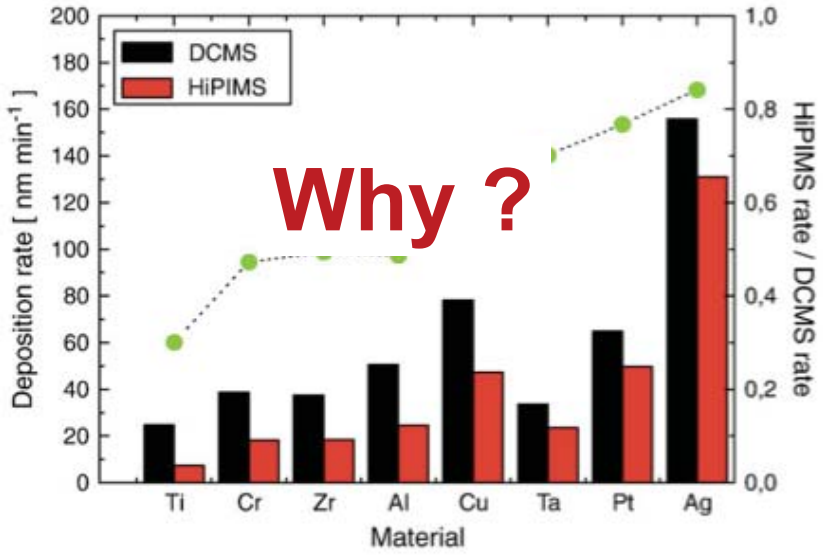
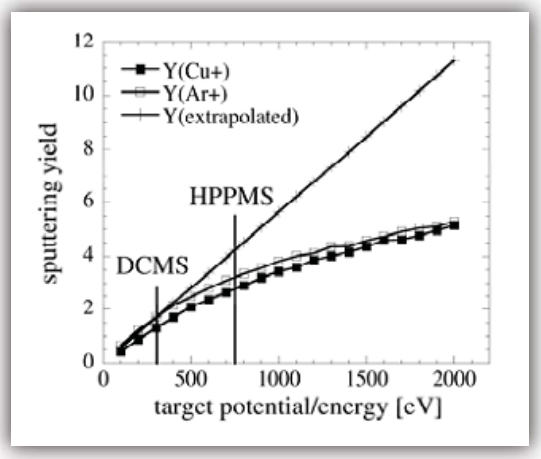


Fig. 1. The deposition rates for DCMS and HiPIMS discharges plotted as bars for the different target materials used (left axis). The deposition rate of HiPIMS over DCMS deposition rate is shown as a scatter plot (right axis).

Samuelsson et al, Surf. Coatings Technol. 205, 591–596 (2010).

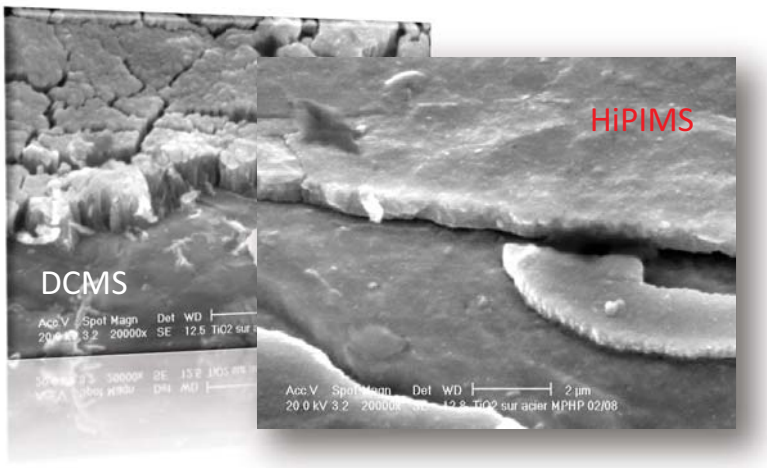
Several reasons to explain the lower deposition rate…

- non-linear dependence of the sputtering yield on the ion energy [1]
- Power losses in switch module
- Transport of the metal, film - forming, ions to the substrate [2 - 6]



1) Emmerlich, Vacuum, 2008
2) Konstantinidis, Appl. Phys. Lett. 2006
3) De Poucques, Plasma Process. Polym., 2007
Lundin, Plasma Sources Sci. Technol., 2008
Bohlmark, Thin Solid Films, 2006
Mishra, Plasma Sources Sci. Technol., 2010

- Increased compactness for the HiPIMS films [1, 2]
  - Comparing the thickness increase/ unit time is misleading.
- Propensity of the HiPIMS discharge to switch towards self-sputtering regime [3-5]



1) Konstantinidis, Thin Solid Films, 2006
2) Konstantinidis, J.Vac. Sci. technol. B, 2007
3) Konstantinidis, J. Appl. Phys., 2006
4) Sarakinos, J. Phys. D., 2008.
5) Alami, Appl. Phys. Lett., 2006

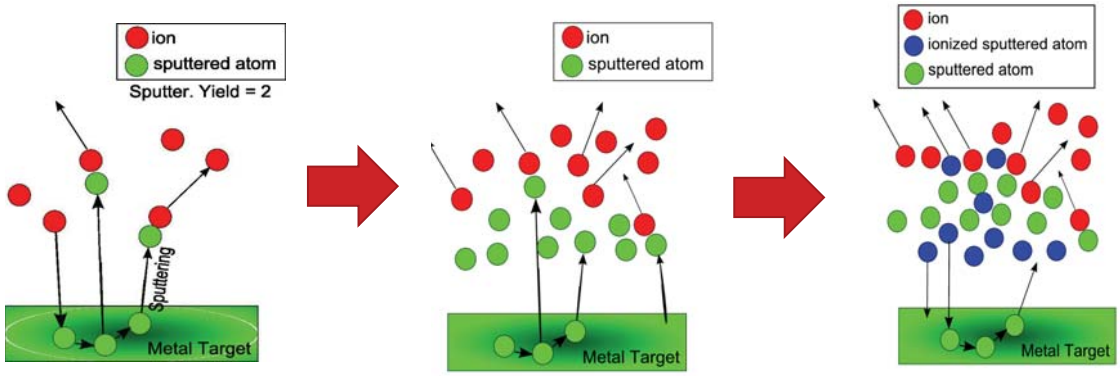
The self-sputtering regime

- When sputtered metal ions sputter the target
- These ions do not contribute to the deposition flux anymore
- The self-sputtering yield is typically lower than the argon-based sputtering mechanism.
- The deposition rate decreases…

$$\Theta \propto \int_{time} \left[I_{G^+} \times Y_{(M-G^+)} + I_{M^+} \left(Y_{(M-M^+)} - 1 \right) \right] dt$$

From *Ar*- to *Self*-Sputtering, the role of the sputtering wind

1. During HiPIMS: large target current (A/cm^2) + high energy of the impinging ions (keV)
2. Large amounts of metal atoms are sputtered (<E_{kin}> ~ sev. eV)
3. Sputtering wind [1] : *exchange of momentum* between sputtered atoms and the Ar atoms (…heating of the argon gas) provokes the rarefaction of the Ar gas.
4. Metal atoms partialy « replace » argon atoms
5. Metal atoms are ionized
6. Metal ions are « attracted » back to the target surface and sputter the metal target (= self-sputtering)



1) Hoffman, JVST A, 1985

Experimental evidence of exchange of momentum between sputtered Ti and background gas atoms

Ti atom speed extracted from LASER spectroscopy experiments.

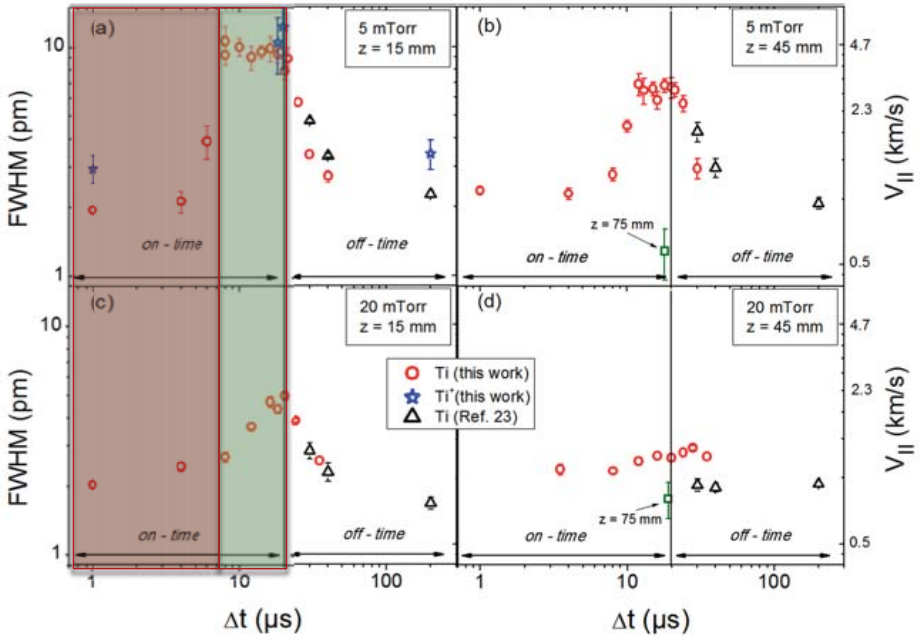


FIG. 5. The FWHMs of the measured Ti fluorescence line determined at several Δt and z at two p_{gas} values after deconvolution with the laser profile. The FWHM data obtained during the HiPIMS off-time are taken from Ref. 23 (triangles). The velocity component v_i parallel to the laser beam (right scale) corresponding to 1/2 FWHM is given for comparison.

M. Palmucci et al, J. Appl. Phys. 114, 113302 (2013).

Experimental evidence of gas heating during HiPIMS discharge

Laser spectroscopy data

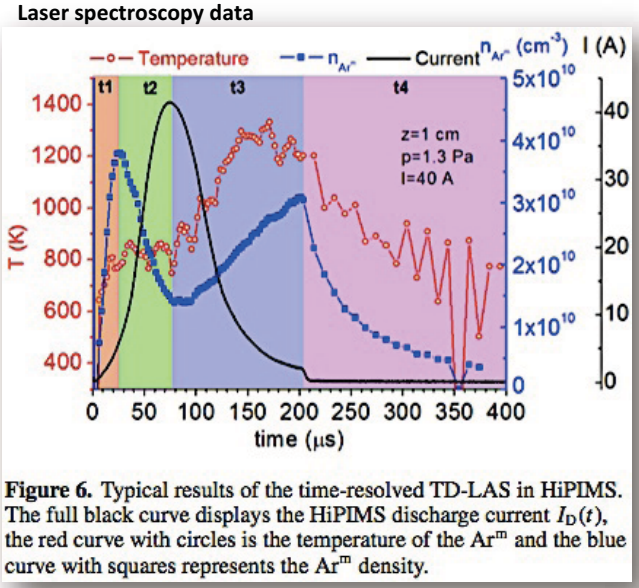


Figure 6. Typical results of the time-resolved TD-LAS in HiPIMS. The full black curve displays the HiPIMS discharge current $I_D(t)$, the red curve with circles is the temperature of the Ar^m and the blue curve with squares represents the Ar^m density.

Vitelaru et al, Plasma Sources Sci. Technol. 21, 025010 (2012).

Time – resolved OES of N2 bands

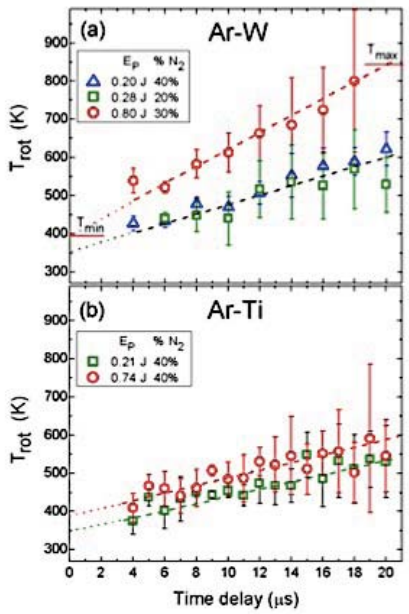


FIG. 5. Time-resolved T_{rot} elevation during a 20 μs HiPIMS pulse in the case of W (a) and Ti (b) sputtering, measured at different E_p, and different N_2 contents. The shown error bars correspond to the Boltzmann plot fitting errors.

Britun et al, J. Appl. Phys. 013301, 013301 (2013).

Modeling of the dynamic plasma-surface interaction during the pulse

1. The current peak is found to precede a maximum in gas rarefaction of the order of $n_{Ar}/n_{Ar,0} \approx 50\%$
2. The dominating mechanism for gas rarefaction is ionization losses, with only about 30% due to the sputter wind kick-out process
   - Ar ion attracted to the target, neutralized, and bouncing back to the plasma bulk
3. During the high-current transient, the degree of sputtered metal ionization reaches 65–75%, and then drops to 30–35% in the plateau phase.
4. The degree of self-sputtering grows from zero at pulse start to a maximum of 65–70% coinciding in time with the maximum gas rarefaction, and then stabilizes in the range 40–45% during the plateau phase.
5. The loss in deposition rate that can be attributed to the back-attraction of the ionized sputtered species is low during the initial 10–20 μ s, peaks around 60% during the high-current transient, and finally stabilizes around 30% during the plateau phase.

Huo et al, Plasma Sources Sci. Technol. 21, 045004 (2012).

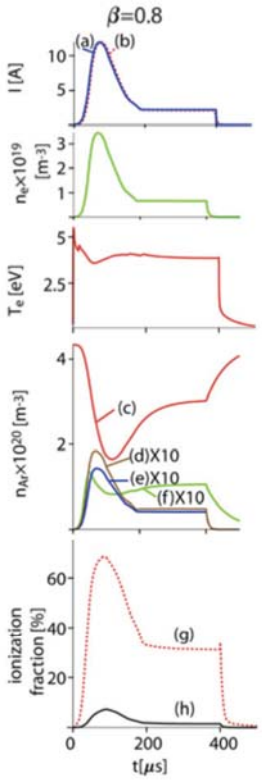


Figure 4. Overview of model results for different fitting parameters. In the three columns, from left to right, $\beta = 0.8$, 0.9 and 1.0. For each β, F_{PWR} is chosen on the best fit curve (b)–(e) in figure 3. *First row*: (a) Experimental discharge current $I_D(t)$, and (b) modeled current $I_{calc}(t)$. *Second row*: $n_e(t)$. *Third row*: $T_e(t)$. *Fourth row*: (c) Total neutral argon gas density n_{Ar}. (d) Argon ion density n_{Ar^+}. (e) Hot recombined argon density n_{Ar^H} (in these runs, $n_{Ar^W} = 0$). (f) Metastable argon density n_{Ar^m}. *Fifth row*: (g) Degree of ionization of the sputtered species. (h) Degree of ionization of argon.

Huo et al, Plasma Sources Sci. Technol. 21, 045004 (2012).

Transport of film forming species to the substrate

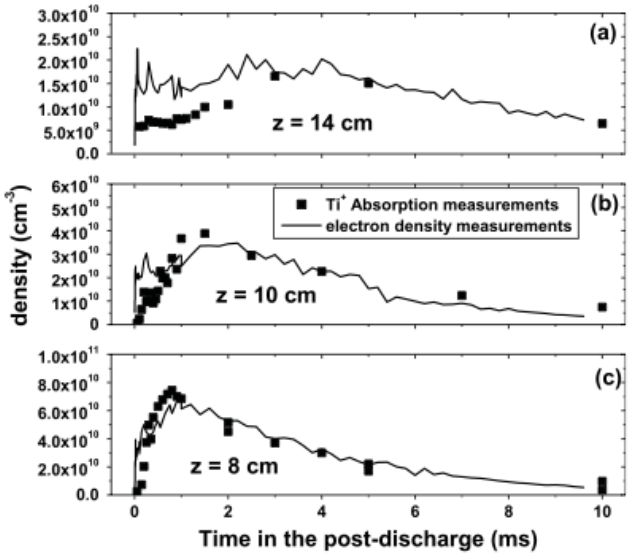
In HiPMS processes, the film forming species = metal ions are produced in the magnetized region.
Metal ions *must travel* from the target region to the substrate surface…

Several parameters influence their transport :

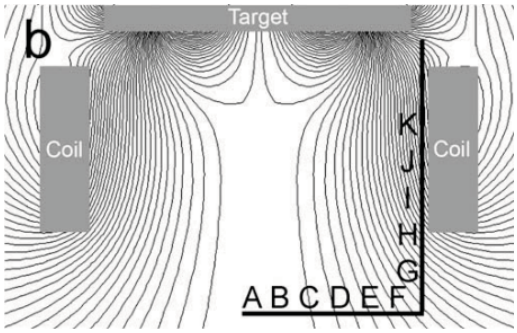
A. The magnetic field architecture is a relevant parameter
B. Sideways ejection of the metal ions is a feature of HiPIMS discharge
C. Time-dependent potential variation prevent ions to reach the substrate

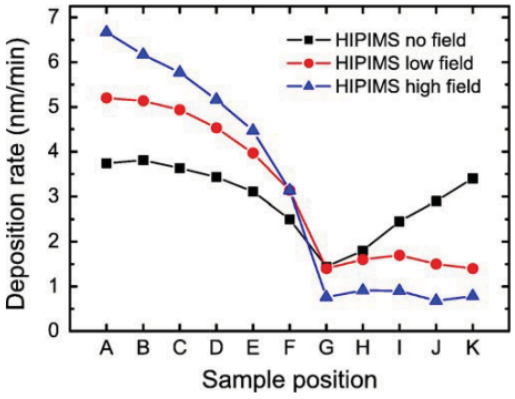
A) Influence of the magnetic field configuration

- Electrons are steered by magnetic field lines
- Metal ions & electrons travel together



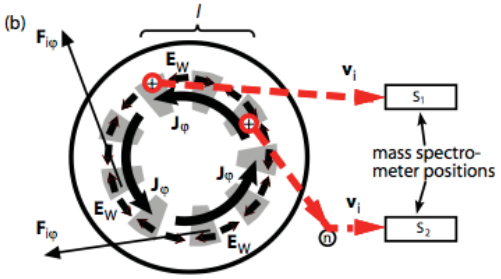
De Poucques et al, Plasma Sources Sci. Technol. 15, 661–669 (2006).





Bohlmark et al, Thin Solid Films 2006.

B) Sideways ejection of the film forming species in HiPIMS plasmas



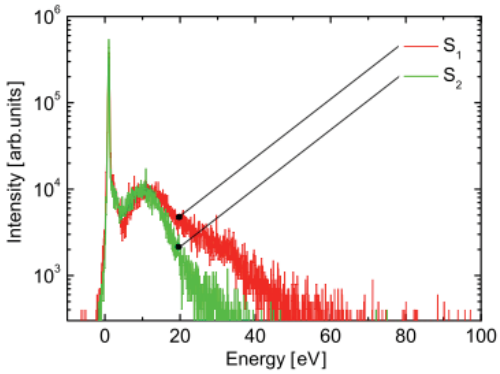
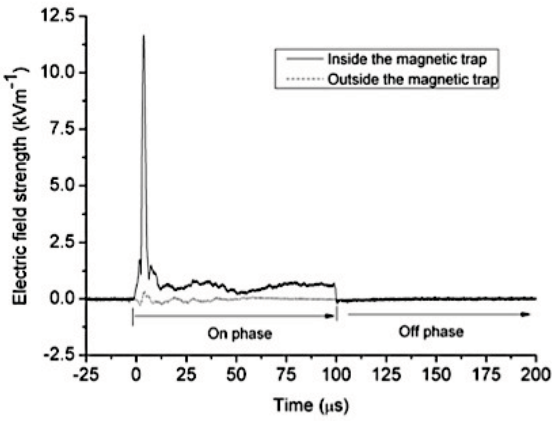
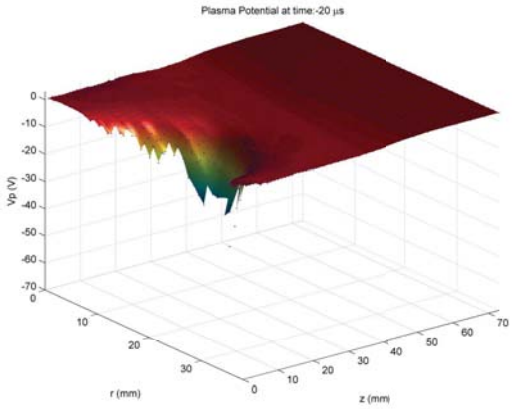


Figure 7. Comparison between Ti^+ion energies from two different sides of the HiPIMS race track, S_1 and S_2, as indicated in figure 1(*b*). The measurements were carried out at 0.80 Pa and $z = 0.01$ m using 500 V discharge pulses.

Lundin et al, Plasma Sources Sci. Technol. 17, 035021 (2008).

C) Time-dependent potential variation prevent ions from reaching the substrate

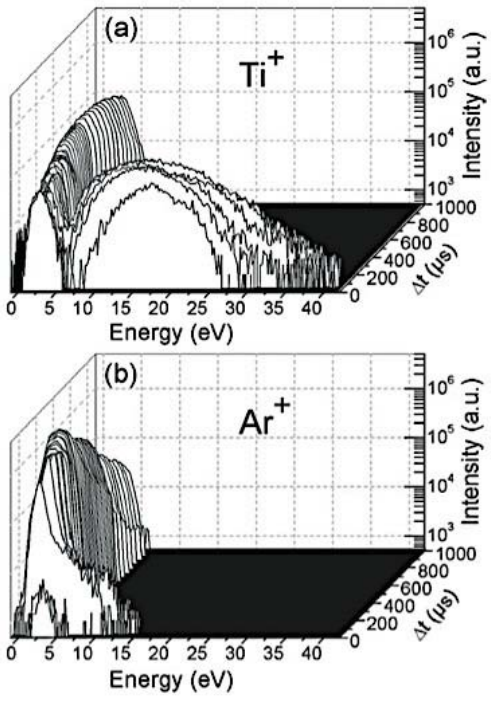




Mishra et al, Plasma Sources Sci. Technol. 19, 045014 (2010).

➔Funnel-like electric field that re-captures the ions and concentrate them on the racetrack.
➔Increased ion bombardment might lead to target surface heating

Plasma dynamics and IEDFs



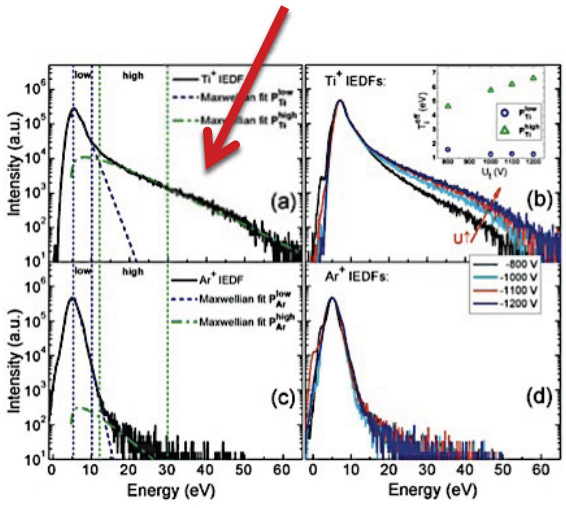
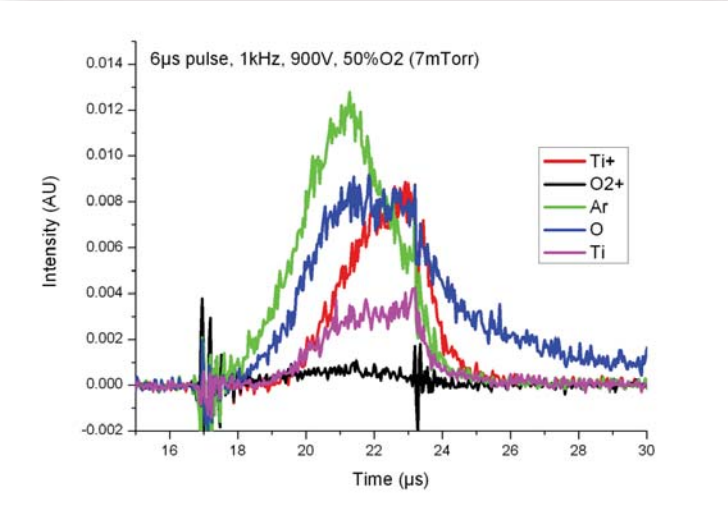
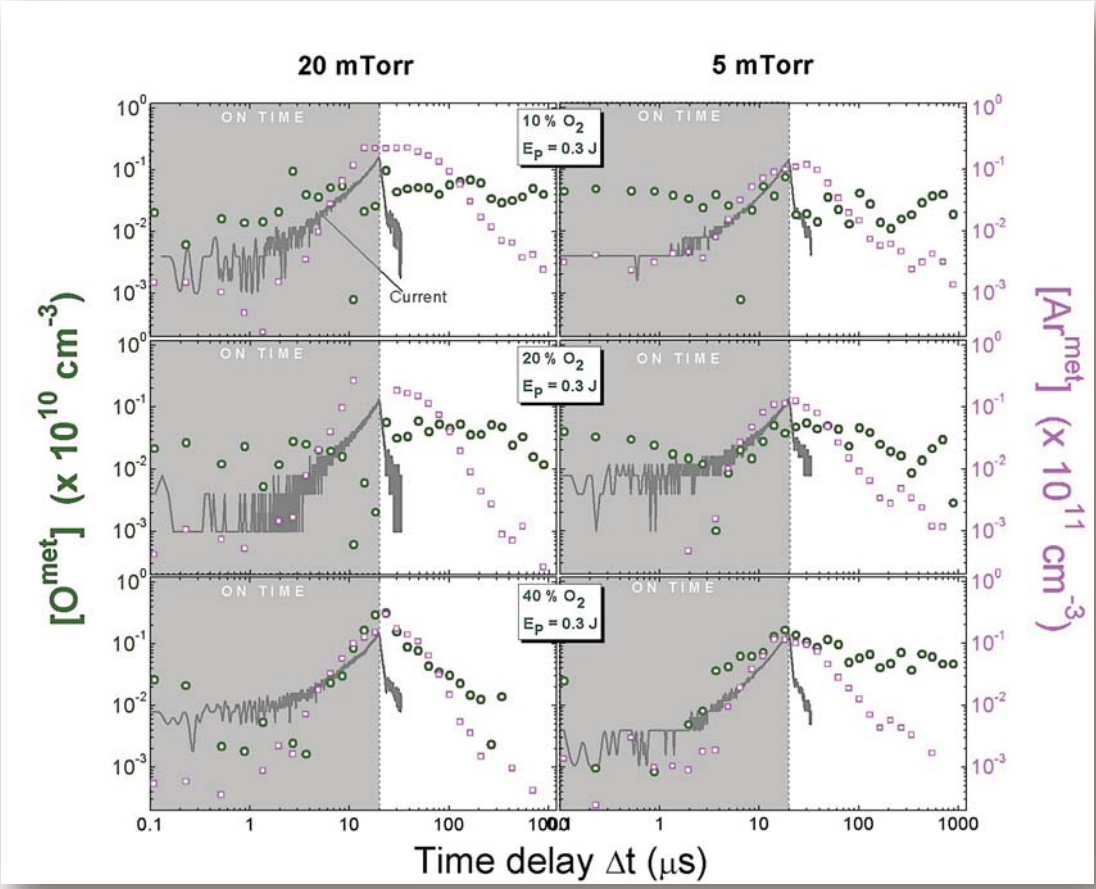


Figure 11. Results of the time-averaged MS measurements of Ti^+ (*a*), (*b*), and Ar^+ (*c*), (*d*) in the HiPIMS discharge. The changes induced by the different applied voltages *U* result in changing the effective Ti^+ temperatures shown for Ti^+ (*b*). Inset: the effective Ti^+ temperatures calculated based on the Maxwellian fit of the data shown in (*b*).

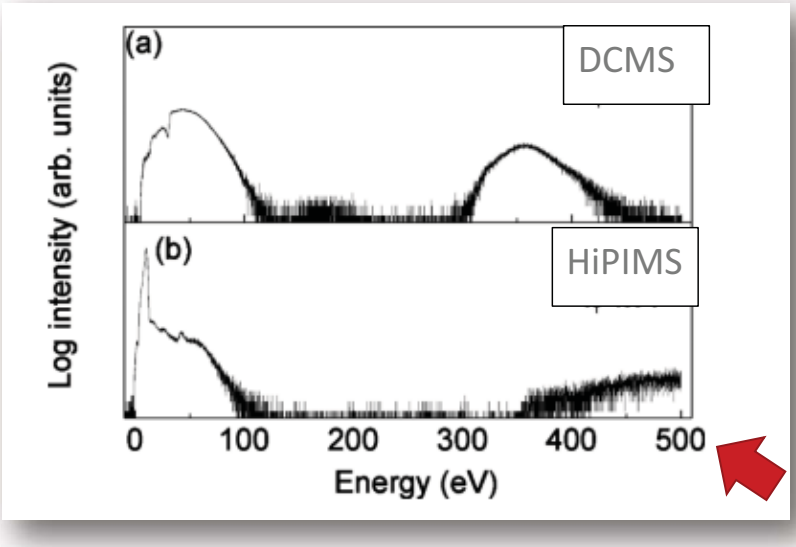
Plasma chemistry in reactive HiPIMS discharges



- $Ti^+ / Ti = 2$
- $O / O_2^+ = 16$
  → O end of pulse
  → O_2^+ merely present in the beginning
- Ar, decreases as Ti and Ti^+ increase
  → sputtering wind, electron cooling



IEDF of O^- during R-HiPIMS



Sarakinos *et al*, J Phys D Appl Phys (2010)

What did we learn so far ?

- HiPIMS discharges can be generated by "replacing" the conventional DC power supply
- Metal ion density and kinetic energy are increased tremendously.
- Film forming species must be transported
- The plasma itself, and the plasma-surface interaction, are dynamic and involve several physical phenomena

- Reactive gas molecules are dissociated and the plasma is chemically very reactive.

➔ Film growth will proceed under intense ion irradiation and in chemically reactive ambient

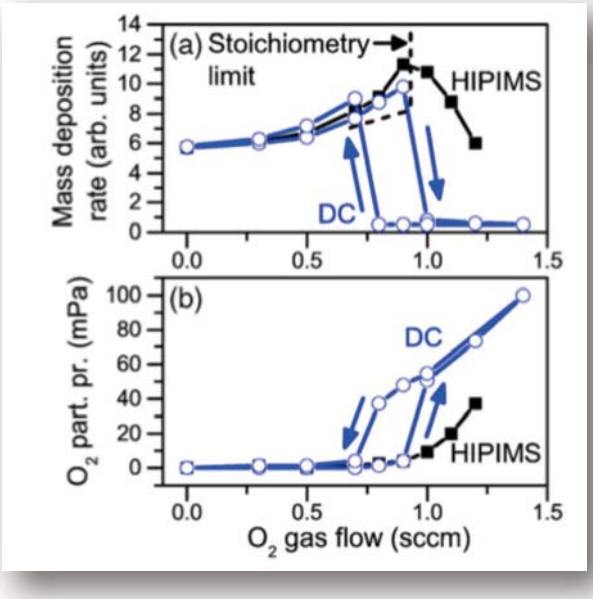
Target poisoning during R-HiPIMS

- Hot topic that is still debated !

- Target poisoning efficiency is modified as compared to reactive DCMS
  - Smoothening of the metallic – poisoned transition
  - Hysteresis width is reduced, sometimes disapears
  - Lower partial pressure needed for poisoning

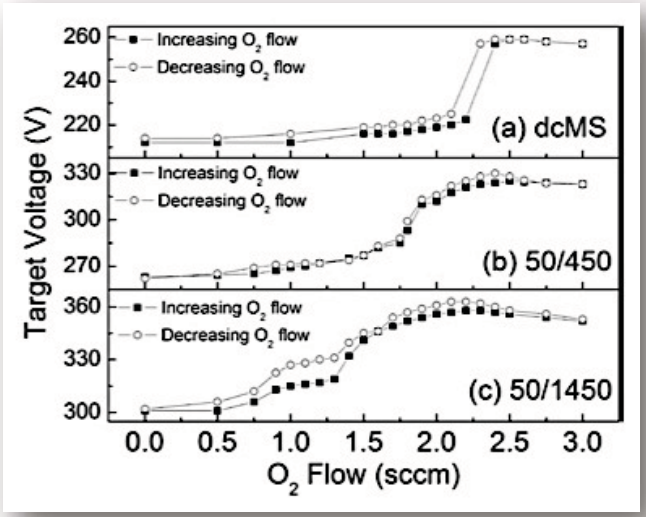
Smoother transition and reduced hysteresis width

Aluminum in Ar/O2



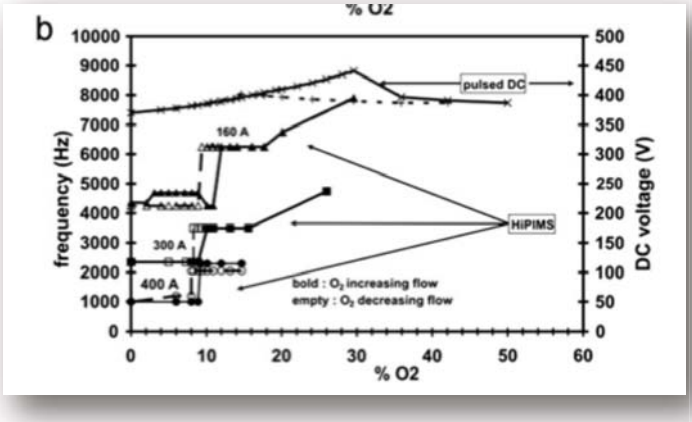
Wallin and Helmersson, Thin Solid Films 516 (2008).

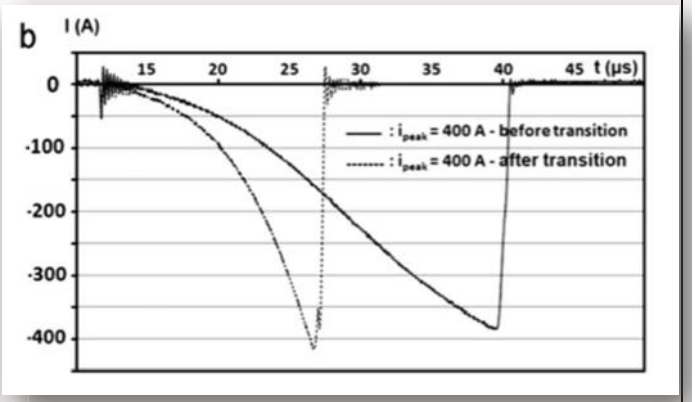
Zirconium in Ar/O2



Sarakinos et al, Surf. Coatings Technol. 202 (2008).

Less oxygen needed to reach poisoning





Lower oxygen partial pressure necessary to reach poisoning +
Modification of the current waveform (increase of the peak current)
➔Suggest improved reactive ion implantation during R-HiPIMS

Nouvellon et al, Surf. Coat. Technol. 206, 3542–3549 (2012).

Possible mechanisms involved during R-HiPIMS

Enhances poisoning (less reactive gas needed to poison)	Reduces poisoning efficiency
Reactive gas dissociation and ionization ➔Reactive gas ions are responsible for target poisoning	**Increased target current + Implantation of target metal ion** ➔Improved target cleaning
Long pulse OFF time ➔Poisoning possible during the long OFF time	**Gas rarefaction** ➔Prevent reactive gas to interact with the target surface
High instantaneous energy input at the target ➔Target heating allows for reactive atoms to diffuse deeper under target surface	
Reduced erosion rate because of self-sputtering ➔Target cleaning would be reduced	

The possibility to grow oxidized films inside the metallic regime

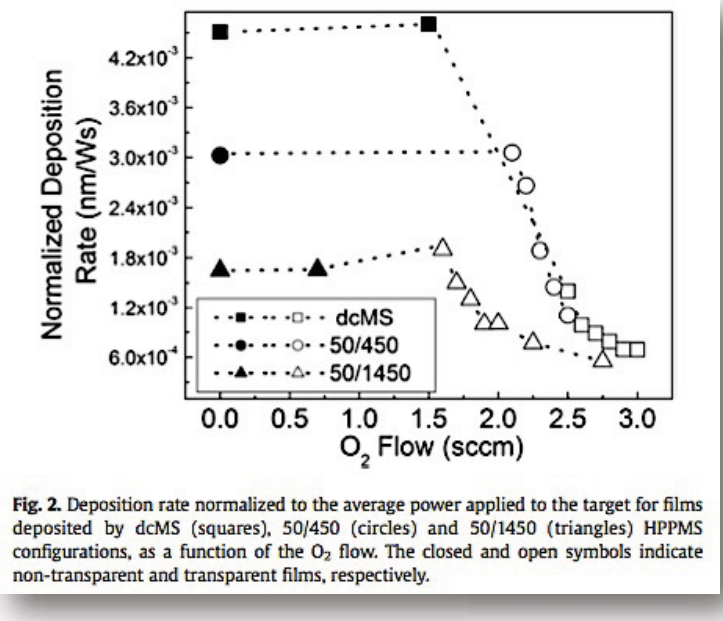


Fig. 2. Deposition rate normalized to the average power applied to the target for films deposited by dcMS (squares), 50/450 (circles) and 50/1450 (triangles) HPPMS configurations, as a function of the O_2 flow. The closed and open symbols indicate non-transparent and transparent films, respectively.

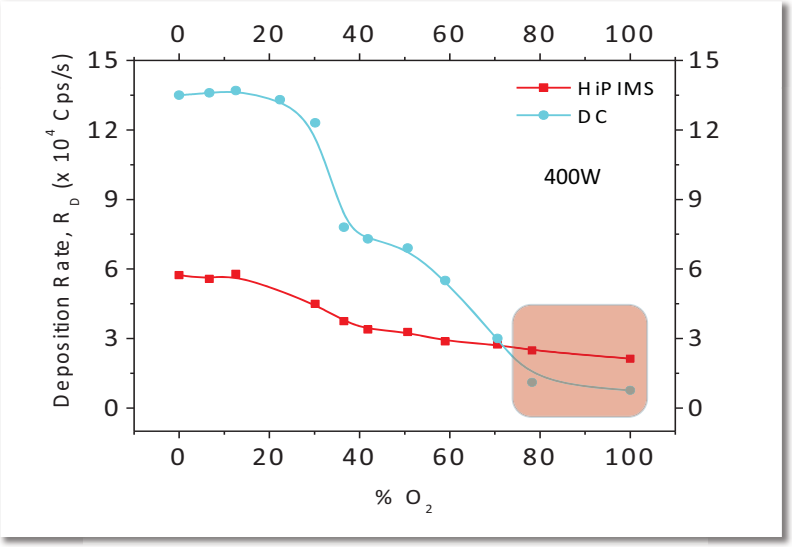
Sarakinos et al, Surf. Coatings Technol. 202 (2008).

The deposition rate in reactive HiPIMS : The peculiar case of tungsten oxide.

Above the DCMS threshold during reactive HiPIMS deposition of tungsten oxide films [1]

The **deposition rate of HiPIMS is increased** as compared to DCMS in the case of

- **Large pulse duration** (= increased time for ionization, = large current)
- **High voltage** (> 1kV)
- Fully **oxidized W target** (O_2% > 80%)

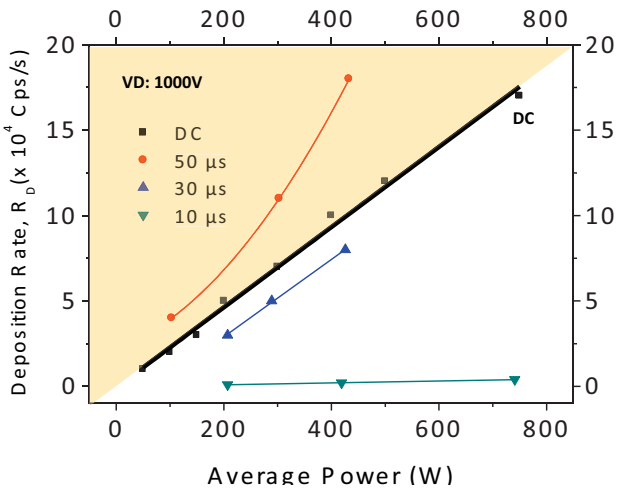


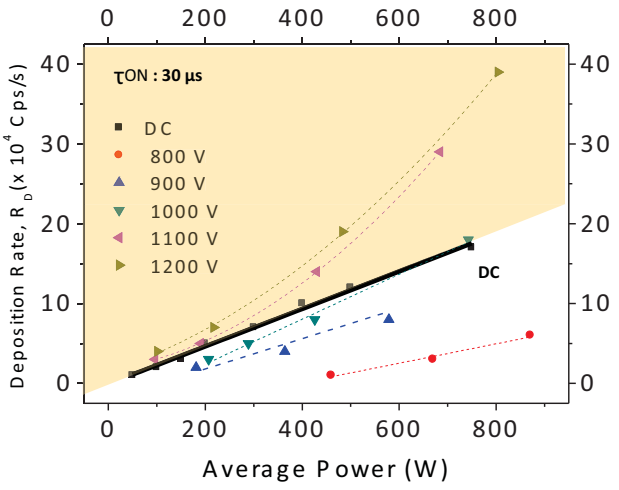
- R_d is measured by XRF
- HiPIMS parameters are :
  - τ_{ON} = 50 µs
  - V_D= 1500 V

Hemberg, J.Vac.Sci.Technol.A, 2012

The deposition rate at 83% in O_2

- Fixed parameters: Ar/O_2 (83% in O_2); 5 mTorr.
- Studied parameters: τ_{ON} and V_D; <P> varied by adjusting the pulse frequency

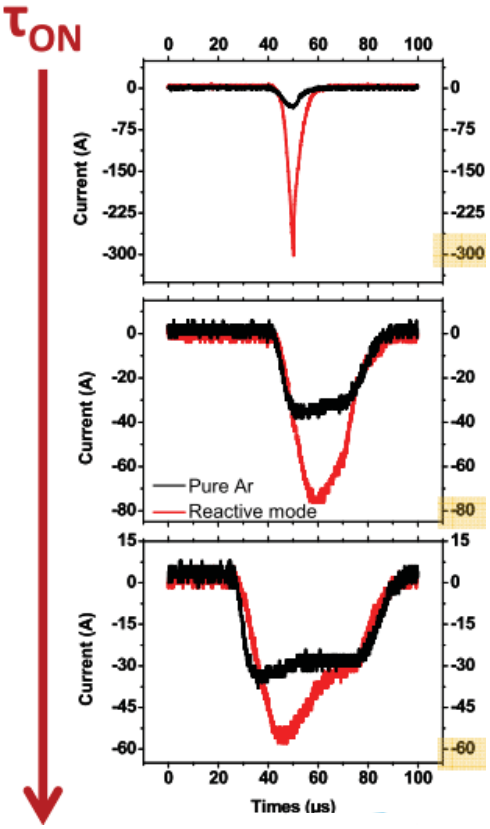




- For large τ_{ON} and V_D , R_D (HiPIMS) > R_D (DCMS)
- In these conditions, **R_D = f(<P>) grows enponentially**

➔ **Another mechanism than sputtering must be present !**

Evolution of the current waveform *vs* pulse duration

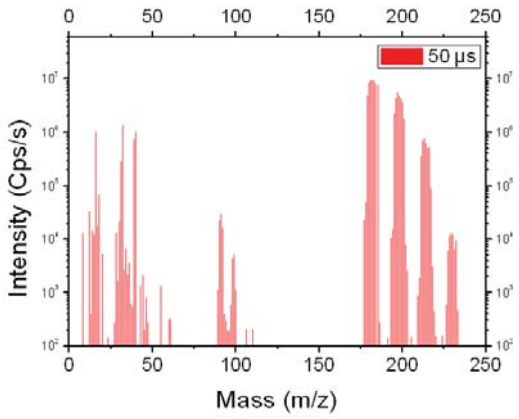


- For large pulses, the current WF during the oxide mode (83% 0_2) looks like the one observed in pure argon discharges
  - Limited poisoning of the target as HiPIMS discharge is used with 1500V , 50 µs pulses ?

Evolution of the plasma chemistry : MS data

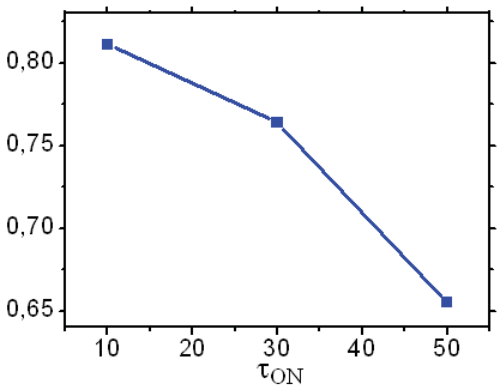
➔The oxidation rate of W–based species in the plasma is an image of the target chemical state

Typical mass spectrum @ 83% of O2



Plasma composition Vs pulse duration

$$\frac{I(W^+)}{\sum_{I}^{x=3} I(WO_X)}$$



- When pulse duration ↑ , the "oxidation" of the plasma ↑ .
- The limited poisoning mechanism is not supported by the mass spectroscopy data.

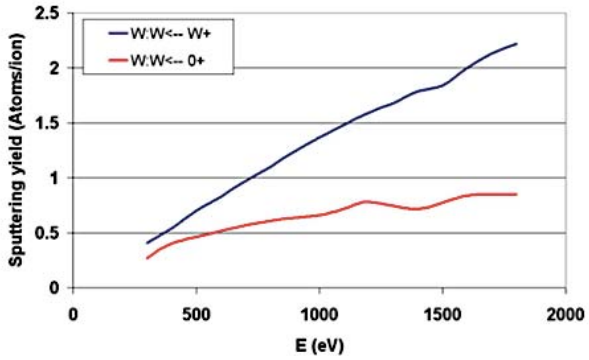
⇒ **Removal of the oxide layer during the pulse is likely to be the mechanism responsible for the increase of R_D**

Towards evaporation-assisted HiPIMS

- If we only consider sputtering,

⇒ **R_D increases « linearly »** with the voltage

TRIM simulation of the sputtering yields



- During evaporation experiments

⇒ **R_D scales <u>exponentially</u>** with the temperature (power) [1]:

$$\Phi_e = 3.513\times10^{22}\frac{P_o \exp(-\Delta H_e/RT)}{\sqrt{MT}}$$

1) Ohring, Materials science of thin films, Academic Press

Finally, why only for high O_2 contents ?

- Estimation of the temperature of the target uppermost layer (10 nm; 10^{-4}g).
  - ΔT_{surf} can be roughly estimated by

$$\Delta Q = m\, C_p\, \Delta T \quad \text{(Heat transfert)}$$

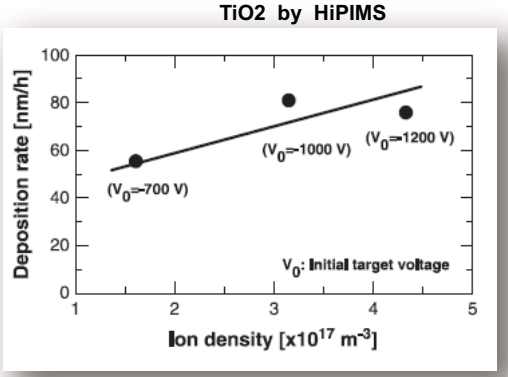
- Assuming 50 kW delivered to the target in 30µs

	HiPIMS (DC)	
	Δ T / °C	Boiling p./ °C
W	3034 (24)	5555
WO_2	1364 (11)	1730
WO_3	2197 (18)	1700
TiO	822 (7)	3227
TiO_2	1220 (10)	3000

ΔT_{surf}(HiPIMS) WO_3 > Boiling P.

Evaporation is likely in this particular case

TiO2 by HiPIMS



Jing, Surf. Coat. Technol. 2011

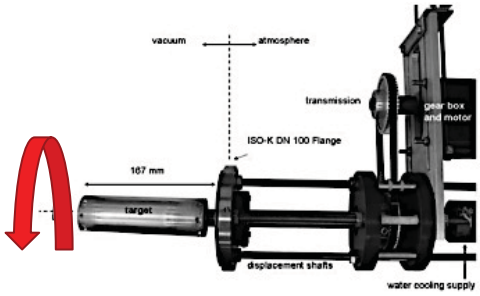
What do we get on the substrate ?

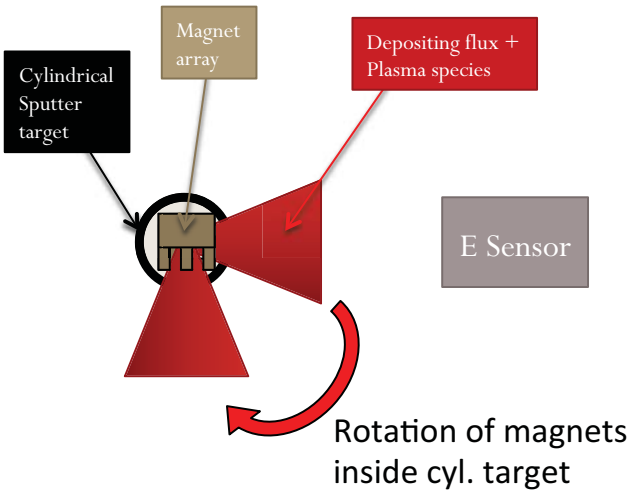
Energy flux measurements at the substrate location

Energy flux measurements @ the substrate location

Specially designed energy flux probes [1,2]

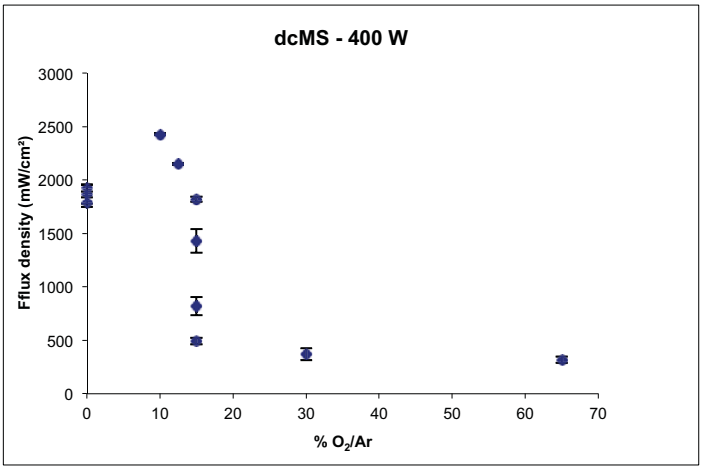
- Planar magnetron target
- Cylindrical rotating magnetron target [3]
  - Allows angle-resolved measurements [4]



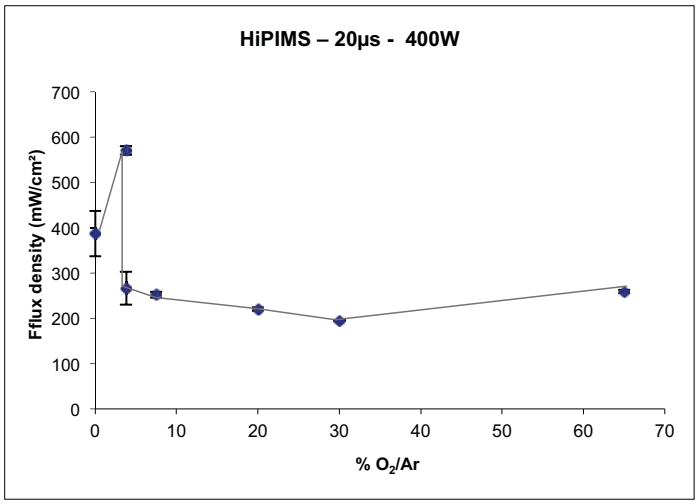


[1] Stahl *et al,* Rev. Sci. Instrum. (2010)
[2] Bedra *et al*, J. Phys. D: Appl. Phys. (2010)
[3] De Gryse *et al*, SVC proceedings (2007)
[4] Leroy *et al*, J.Phys. D. Appl. Phys (2011)

HiPIMS of a planar Ti target
- Energy flux as a function of the oxygen flow



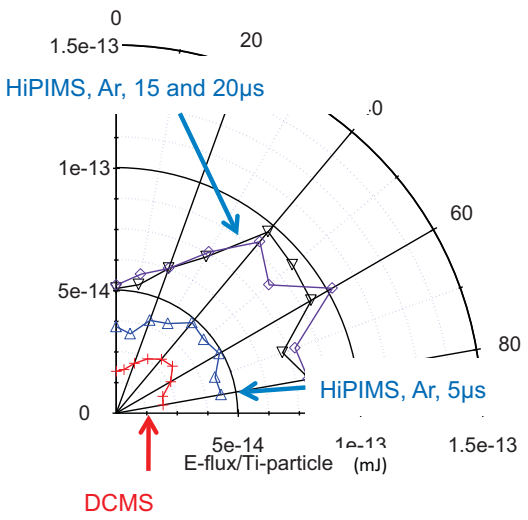
DCMS and HiPIMS
400W, 0.8 Pa

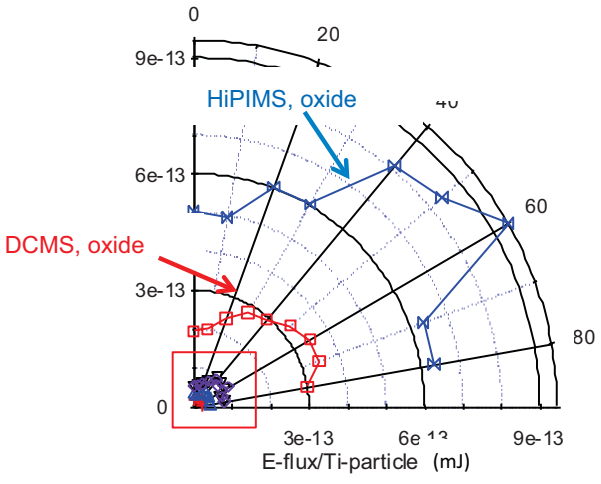


- E decreases in the oxidized regime
  ➔ Decrease of R_d (~ / 10)
- Decrease of E_{sub} (~ / 4 times)
  ➔ the flux of depositing material is not the only source of energy
- E (dcMS) > E (HiPIMS)

Energy flux measurements on a rotating cylindrical magnetron target : *Energy per adparticles*

Energy per adparticle ⇒ E_{ad} = E flux / deposition rate
Dep. rate by RBS





Leroy et al, J.Phys. D. Appl. Phys (2011)

Energy flux measurements : what do we learn ?

1. $E_{ad\ (HiPIMS,\ 20\mu s)} > E_{ad\ (HiPIMS,\ 5\mu s)} > E_{(\mathbf{DCMS})}$
   - Ionization rate of sputtered vapor increases with pulse duration
   - IEDF extended to higher kinetic energies
   - Secondary e^-
   - Photons
   - Multiply charged ions reflected from the target (?)
   - …

2. The highest energy per adparticles is measured for oxide regimes (DCMS and HiPIMS)
   - Presence of O^- emited from the target with $E_{kin} = V_d$

3. $E_{ad\ (\mathbf{HiPIMS,\ oxide})} > E_{ad\ (\mathbf{DCMS,\ oxide})}$

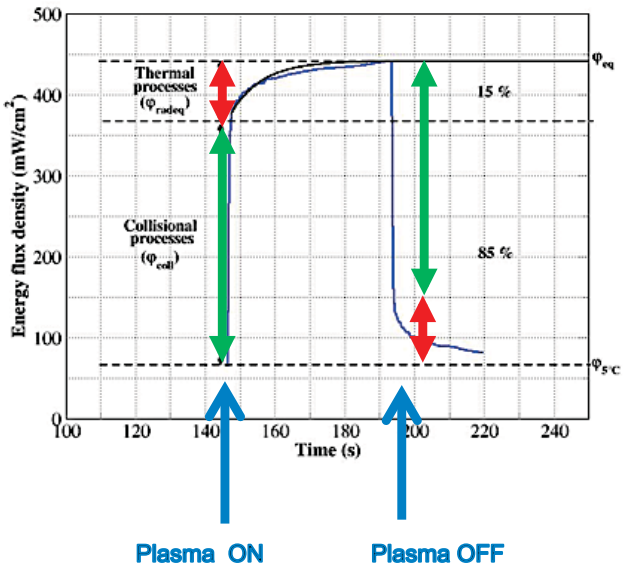
Some insights on the target temperature thanks to energy flux measurements

Thermopile – based probe

Allows to distinguish:

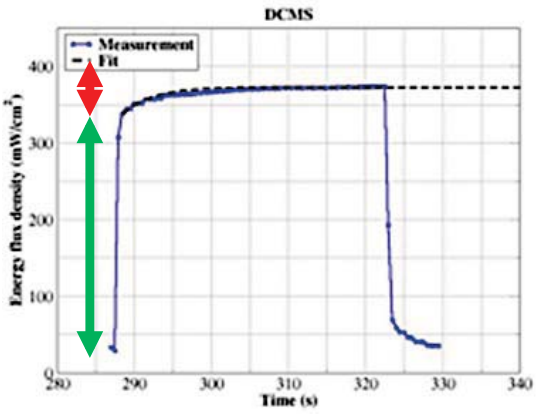
1. Rapid processes
   - Plasma related contributions
2. Slow processes
   - IR emitted by gradually heating target surface
     → **Target** bombarded by plasma ions.

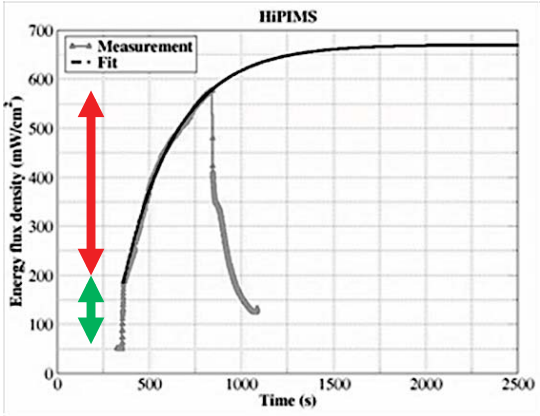
Typical Energy Flux Vs time signal



Cormier et al, Thin Solid Films (2013).

Evaluation of the target temperature





- Target temperature is estimated from fit :
  - 330 °C for DCMS
  - **870°C** for HiPIMS

Evolution of the thermal contribution with process parameters

Discharge type/ power (W)	Plasma contrib. (mW/cm2)	IR contrib. (mW/cm2)	Total energy flux (mW/cm2)	Fraction attributed to IR emission	Target temp. (°C)
B – DCMS 100W	124	14	138	9 %	211
B – DCMS 200W	191	23	214	10 %	269
B-DCMS 400W	315	45	360	12 %	362
UB – pDCMS 400W	2231	69	2300	3 %	705
B-HiPIMS 400W	160	607	667	76 %	870

What did we learn ?

- Target is heated as plasma ions bombard the target
- Hot target emits IR photons which bombard the growing films

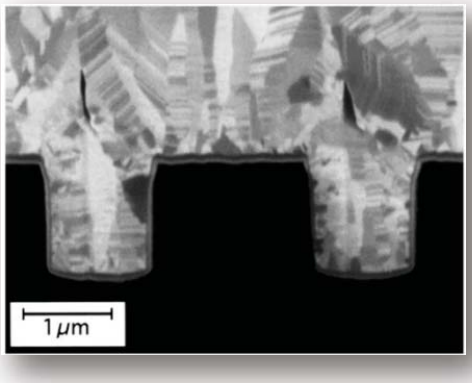
- In some case (HiPIMS, B-Field) this contribution is more than significant and could be invoked to explain:
  - Some results obtained when characterizing the thin films.
    - Emissivity of the film might become a key parameter
  - The "above the DCMS-threshold" deposition rates measured in HiPIMS plasma (the case of tungsten trioxide)

What about the film properties ?

- Conformation deposition over trenches
- Film densification
- Modification of the phase constitution and microstructure

Conformal deposition over trenches

Conformal deposition



Kouznetsov et al, Surf. Coat. Technol.,1999

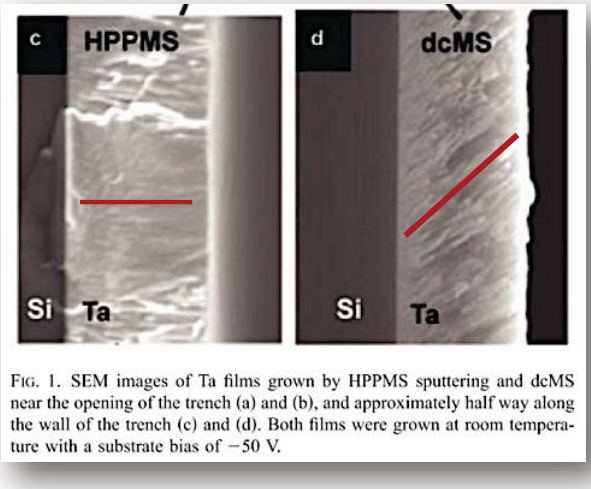
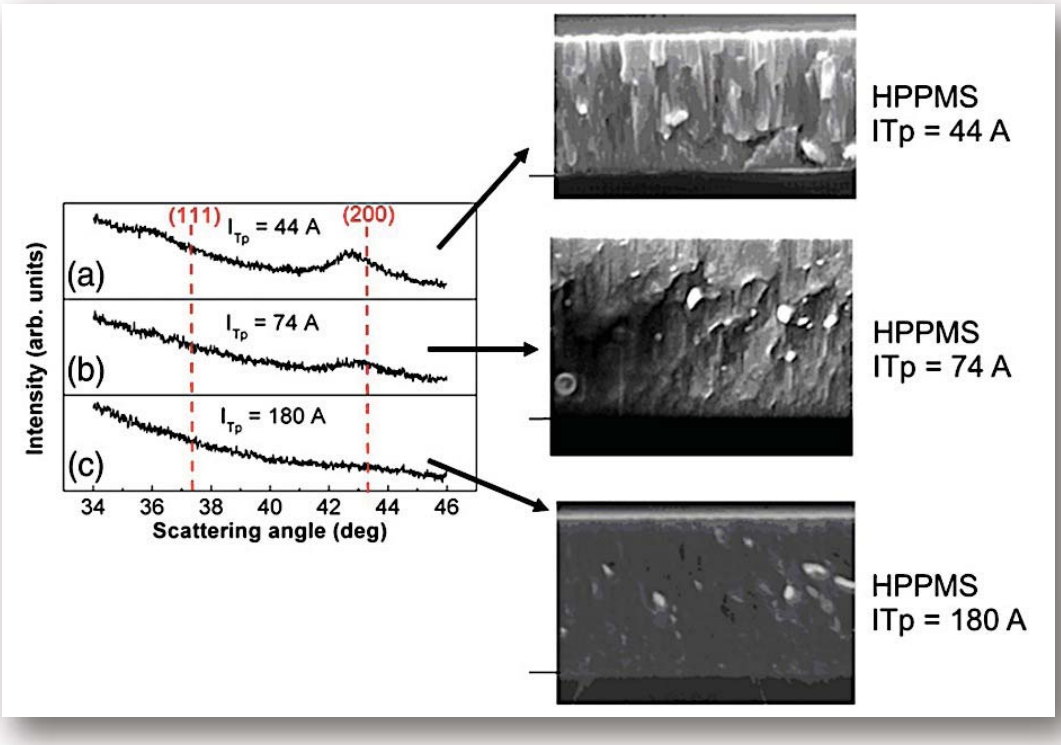


FIG. 1. SEM images of Ta films grown by HPPMS sputtering and dcMS near the opening of the trench (a) and (b), and approximately half way along the wall of the trench (c) and (d). Both films were grown at room temperature with a substrate bias of −50 V.

Alami *et al*, JVST A,2007

Microstructure modification (CrN)



Alami *et al*, J. Phys. D: Appl. Phys. 2009

Enhanced film compactness

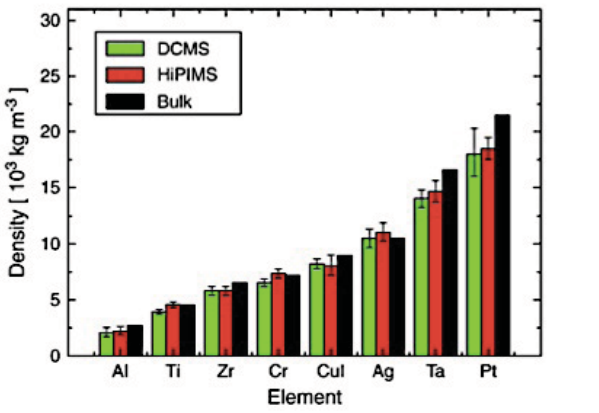


Fig. 3. Thin film density plot for different target materials. The values are calculated for films grown by DCMS and HiPIMS using RBS, SEM and profilometry. The results are compared to the bulk density given in literature.

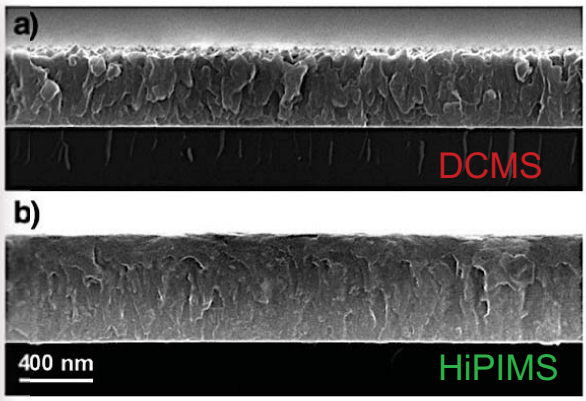


Fig. 4. Cross-sectional SEM image of a Ti sample grown by a) DCMS and b) HiPIMS. The DCMS deposited sample exhibits a porous microstructure and rough surface, whereas the HiPIMS deposited sample exhibits a less pronounced columnar microstructure and a smooth surface. The scale bar applies to both images.

Samuelsson et al, Surf. Coatings Technol. 205, 591–596 (2010).

Interface engineering & wear protection

Interface engineering

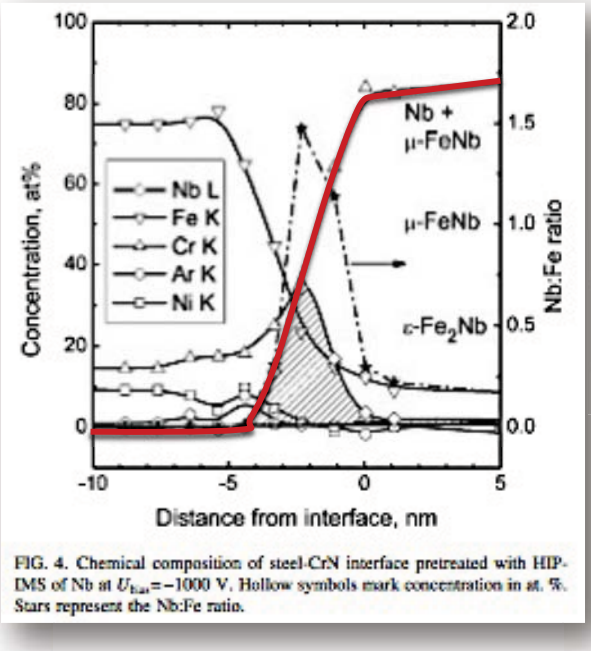


FIG. 4. Chemical composition of steel-CrN interface pretreated with HIPIMS of Nb at U_{bias}=−1000 V. Hollow symbols mark concentration in at. %. Stars represent the Nb:Fe ratio.

Enhancement of wear protection

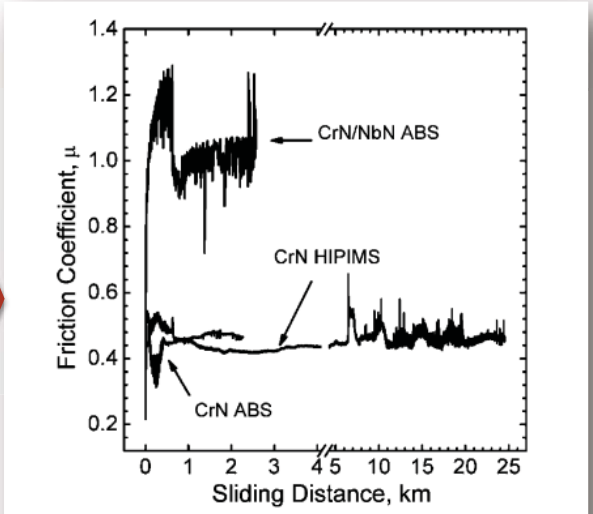


Fig. 5. Friction coefficient of CrN-HIPIMS, CrN-ABS and CrN/NbN-ABS coated discs against Al_2O_3 ball measured in pin-on-disk test.

Ehiasarian, J. Appl. Phys, 2007

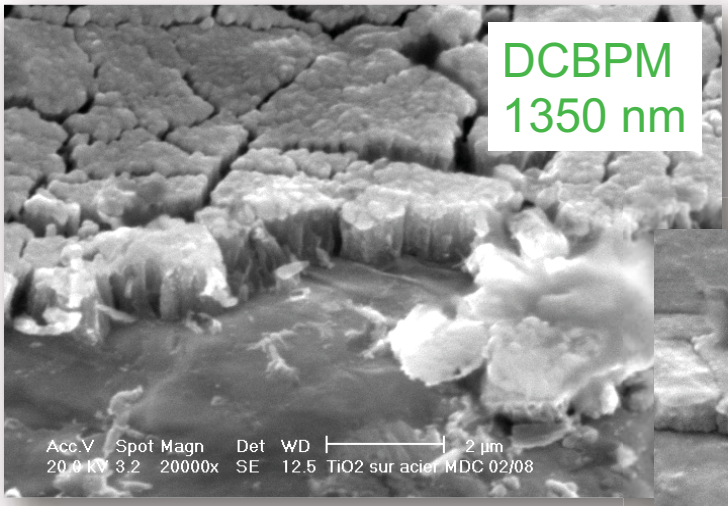
Ehiasarian, Thin Solid Films, 2004

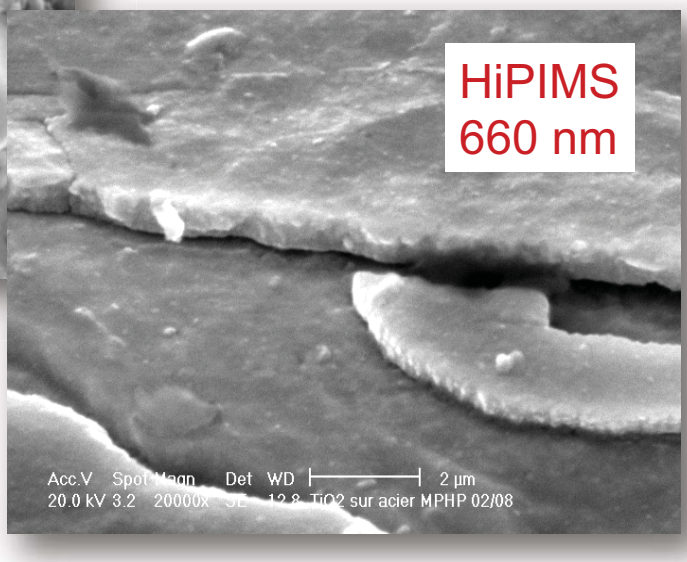
Synthesis of titanium dioxide thin films

- TiO_2 : optical coating and photocatalytic properties [1]
  - Photocatal. activity is optimized for a mixture of anatase + rutile [2]
  - Rutile needs more energy than anatase [3]

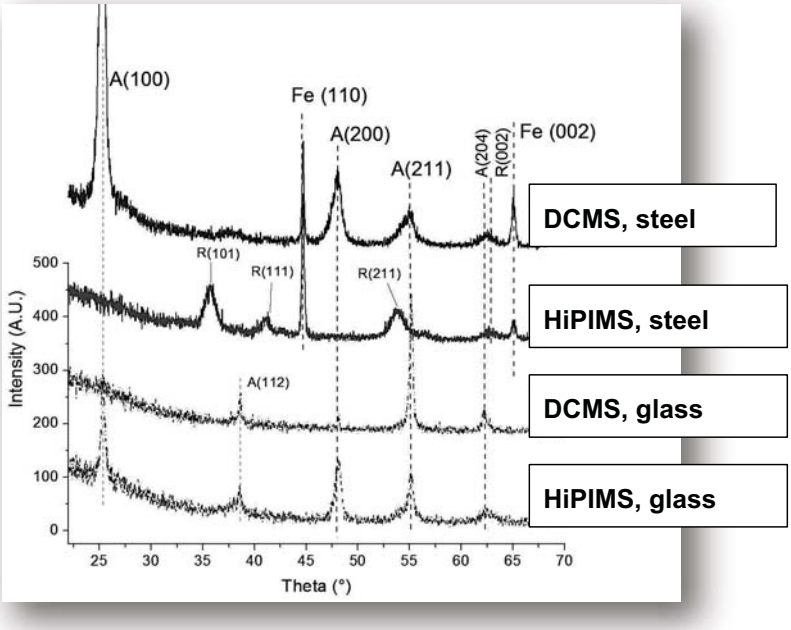
[1] Mills & Le Hunte, *J. Photochem. Photobiol.A Chem.* (1997)
[2] Takawahara et al, *Ang. Chem.Int. Ed.* (2002)
[3] Martin et al, *Thin Solid Films* (1997)

Scanning Electron Microscopy





XRD analysis



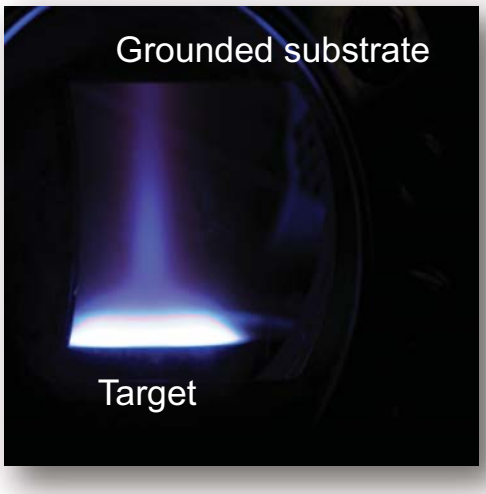
- On grounded steel
  HiPIMS : RUTILE
  DCMS : ANATASE
- On (floating) glass
  ANATASE

Rutile is the high-temperature phase ! [1]

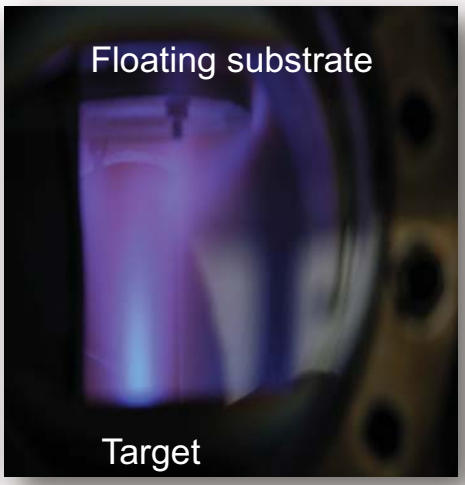
⇒ Energy supplied to the film in HiPIMS

[1] N. Martin *et al*, Thin Solid Films (1997)

Grounded *vs* floating substrates



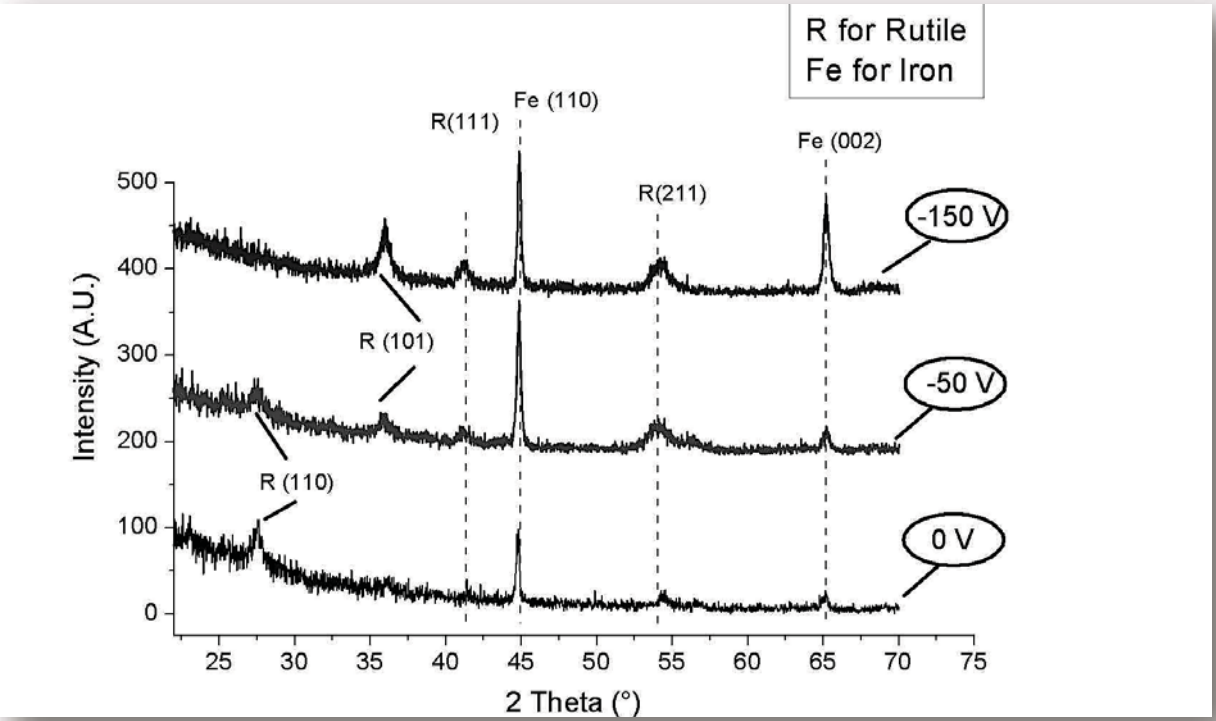
Well-defined plasma column



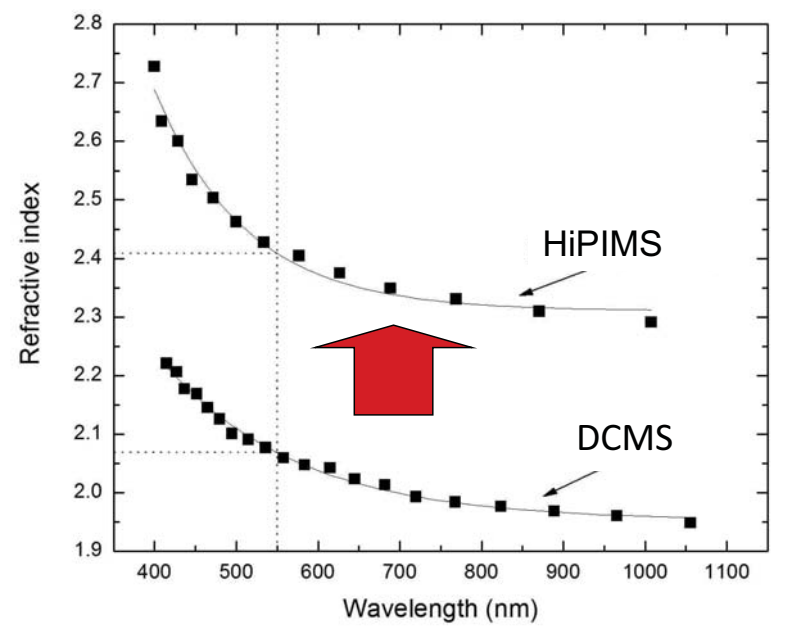
Plasma cloud around the substrate

During HiPIMS, ion and electron transport is apparently influenced by the substrate electrical conditions

Influence of substrate bias



Optical properties, refractive index

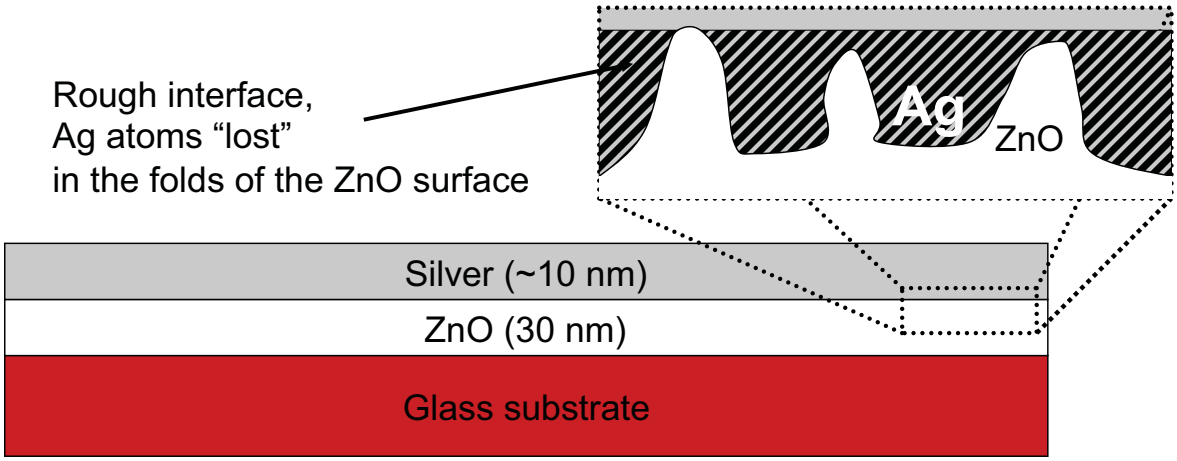


n(HiPIMS) > n(DCMS)

On glass, both deposition processes give phase pure anatase films
→ higher index attributed to film densification by HiPIMS

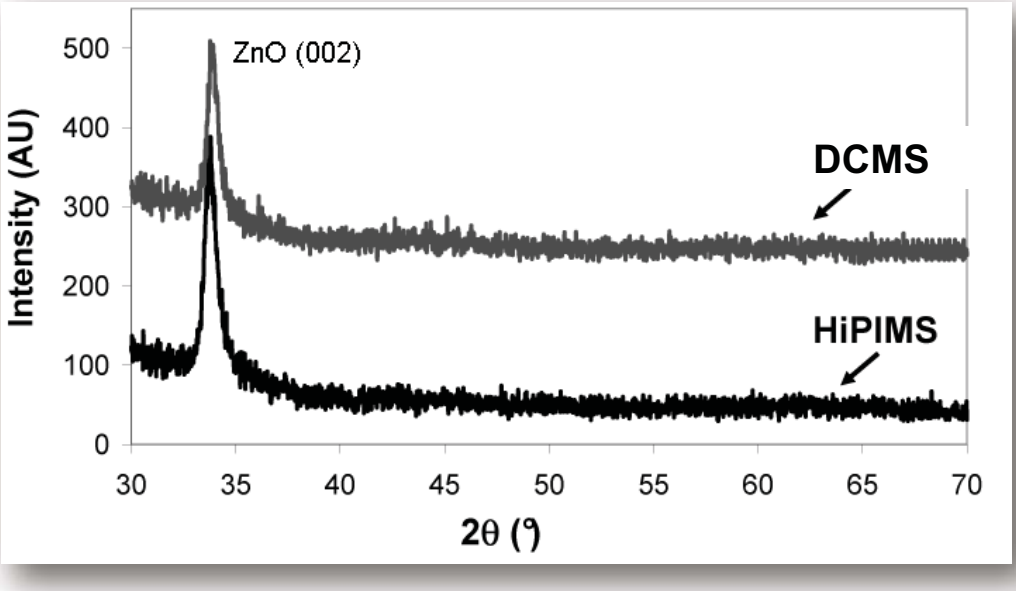
Application of ZnO coatings

- Used as seed layer for optical low-E, silver-based, multilayer coatings [1]
- ZnO must be smooth and well crystallized to obtain low emissivity



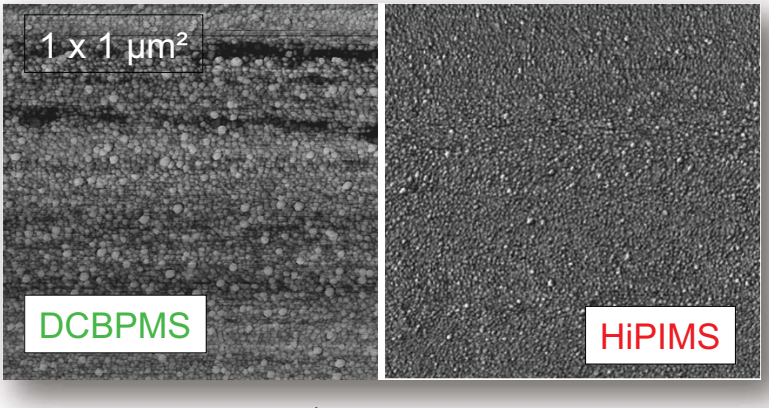
[1] M. Arbab, Thin Solid Films (2001).

Phase constitution



Technique	Grain size (nm)
DCMS	15
HiPIMS	13

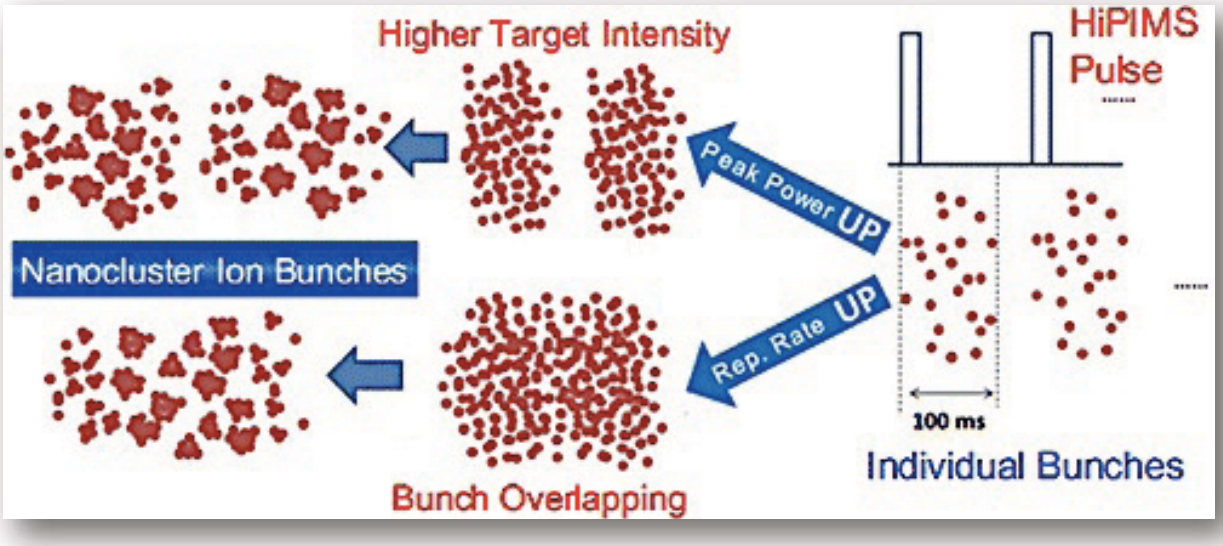
Surface topography by AFM



Deposition technique	Peak-to-valley roughness (nm)
DCMS	6
HiPIMS	4

→ Smoother surface with HiPIMS

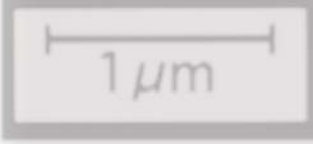
HiPIMS as a tool to produce nanoparticles



Zhang et al, J. Phys. Chem. A 117, 10211–7 (2013).

Concluding remarks

- HiPIMS technology belongs to the I-PVD family
- It provides more knobs to the thin film engineer to design coatings with improved functionalities
- However, the process involves complex physical phenomena
- And the deposition rate is reduced
- Although the process itself can be implemented easily
- Taking full benefit from it requires optimization of the working environment



But … non-conformal deposition is still cool !

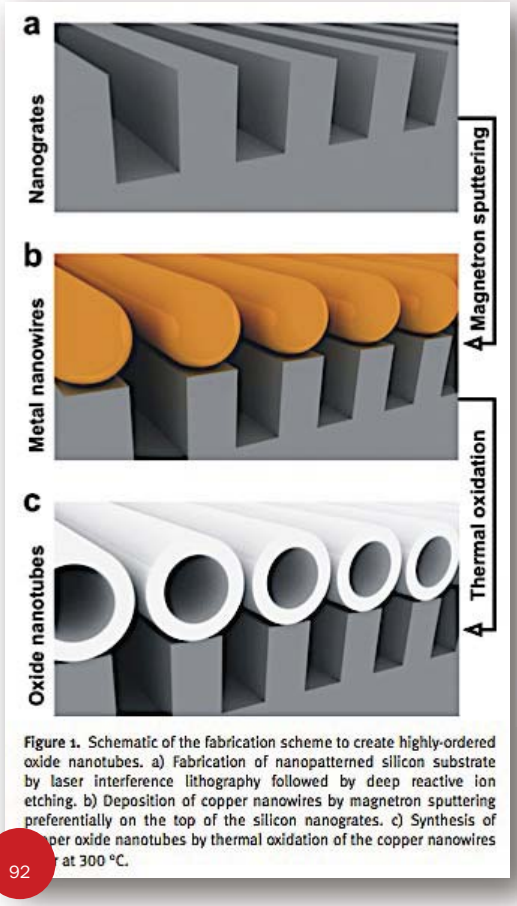


Figure 1. Schematic of the fabrication scheme to create highly-ordered oxide nanotubes. a) Fabrication of nanopatterned silicon substrate by laser interference lithography followed by deep reactive ion etching. b) Deposition of copper nanowires by magnetron sputtering preferentially on the top of the silicon nanogrates. c) Synthesis of [illegible]per oxide nanotubes by thermal oxidation of the copper nanowires [illegible] at 300 °C.

El Mel et al, Small (2013).