Diagnostic of energy transfers in plasma sputter deposition: a way to investigate the sputtering process and the film growth

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I. Outline

Energy transfers are critical for the control of thin films/modified surfaces properties…

…and can give interesting insight into mechanisms taking place at the substrate and governing the sputtering process.

I. Energetic contributions in magnetron sputter (MS)deposition

II. Probes to measure the energy influx at the substrate

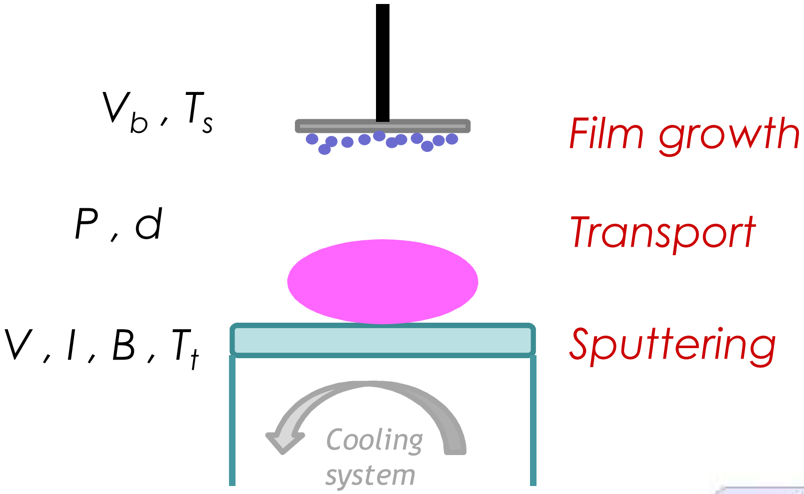
III. Total energy transfer/thin films properties

IV. Detection of chemical reactions in the growing film

V. IR radiation contribution: target temperature control

I. Energetic contributions in MS deposition

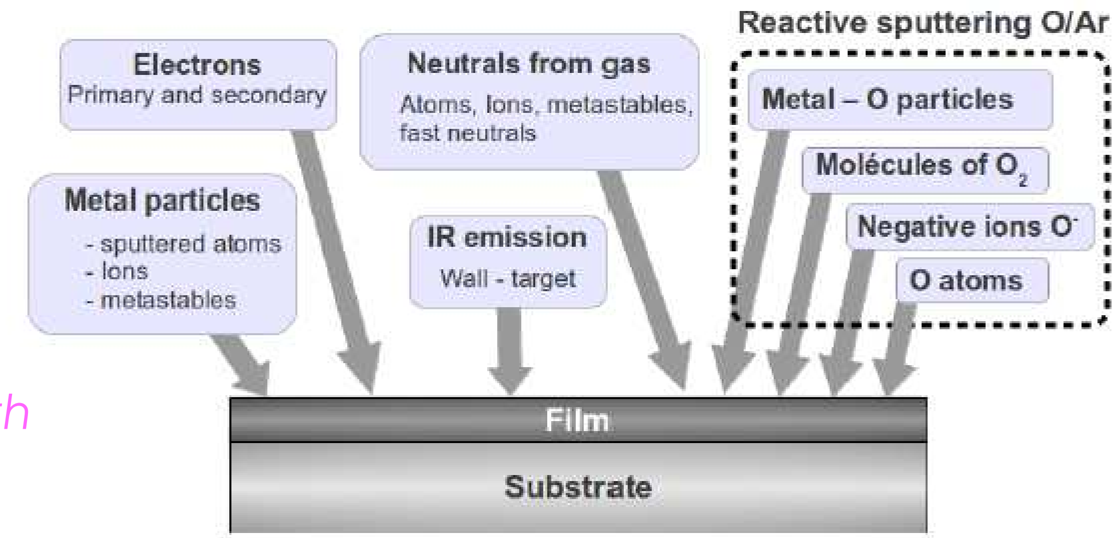
Various particles interact with the growing film



- *Charged particles (Me+, e-, G-,G+, MeG+ etc.)*
- *Neutrals (Me, G)*
- *Radicals, molecules*
- *« Radiations (IR etc.) »*

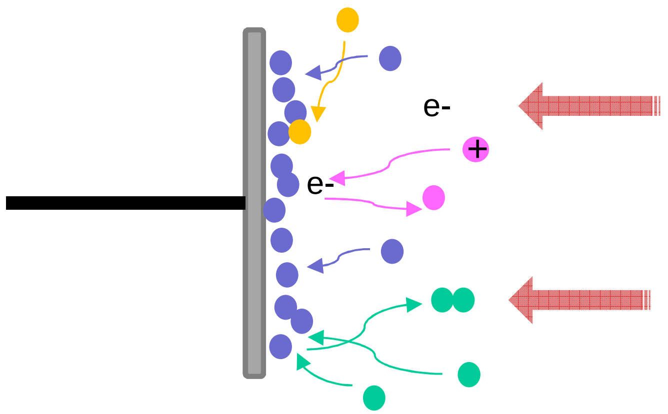
Depositing particles

Particles assisting the growth



I. Energetic contributions in MS deposition

Various elementary mechanisms are responsible for the energy transfer (involved in the film growth/surface modification)



Elastic collisions (kinetic energy transfer)

Condensation
Recombination
Chemical reaction
Radiation absorption

These contributions exhibit various kinetics:

- *collision transfers (fast)*
- *chemical reactions*
- *IR radiation from the heated target (kinetic of the heating process)*

$$P_{in} = \int \varphi_{tot}.dS = \int \left(\varphi_{rad} + \varphi_{ch} + \varphi_{n} + \varphi_{film} + \varphi_{react}\right).dS$$

I. Energetic contributions

Global transferred energy is expected to determine the final film/surface properties

conventional normalized energetic parameter is the E_{tot}/At

Correlation with data from plasma diagnostics allows to evidence the species playing the main role in the energy transfer

determination of the specy driving the growth/modification ?

Evolution of the global energy vs a process parameter or vs time

information on mechanisms involved in deposition/ modification/sputtering processes

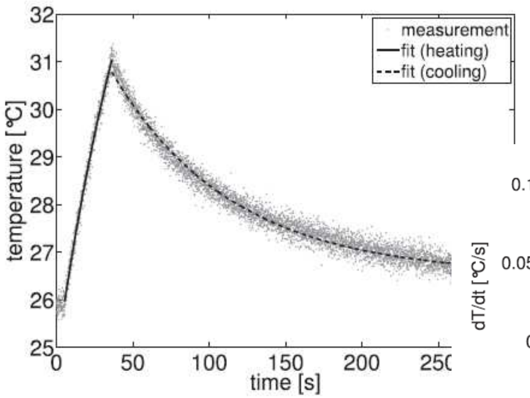
II. Probes

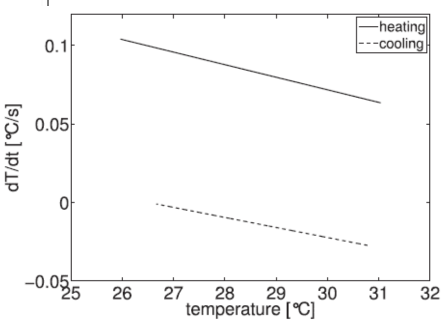
Calorimetric probes

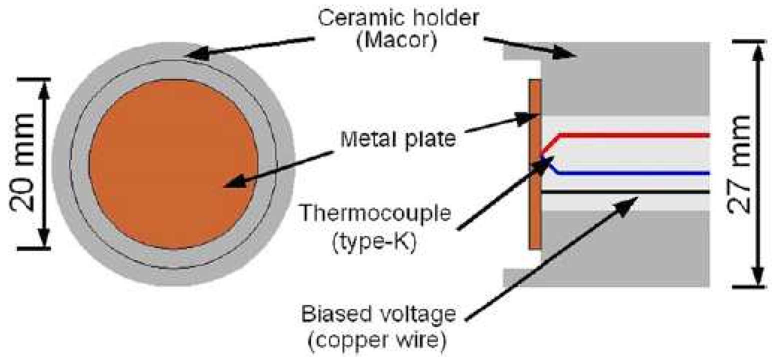
(D.J. Ball 1972, J.A. Thornton 1978, R. Wendt 1997, H. Kersten since 1994 etc.)

- *Temperature measurement*
- *Recording of the thermogram during the heating and cooling steps*

$$J_{\text{in}} = \frac{\dot{Q}_{\text{in}}}{A_{\text{p}}} = \frac{m_{\text{p}} c_p}{A_{\text{p}}} \left[\left(\frac{\mathrm{d}T_{\text{p}}}{\mathrm{d}t} \right)_{\text{heat}} - \left(\frac{\mathrm{d}T_{\text{p}}}{\mathrm{d}t} \right)_{\text{cool}} \right]_{T_{\text{p}}}$$







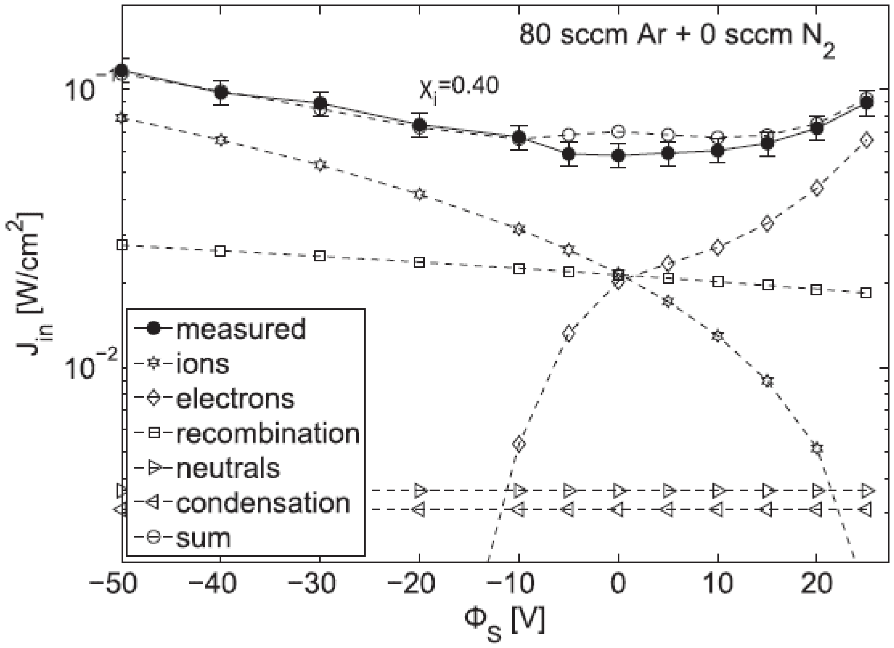
H. Kersten et al (Vacuum 63 (2001) 385)

Advantages:
Cheap
Easy to implement
<u>Can be biased</u>

Drawbacks:
Poor time resolution (at least 2 min)
A posteriori influx determination
requires Cp knowledge (delicate calibration)

II. Probes

Example of the study of c-BN film deposition by RF magnetron sputtering



S. Bornholdt et al (J. Appl. Phys. 112 (2012) 123301)

The calorimetric probe being used as a Langmuir probe, energetic contributions can be evaluated from ion and electron currents and compared to the measured values of the influx

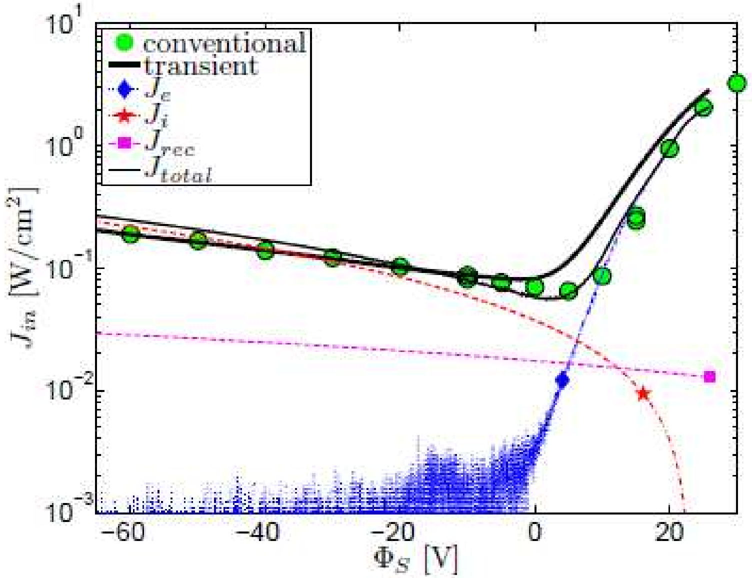
- The energy transfer is mainly due to charged particles, contribution of neutral sputtered atoms (kinetic and condensation energies) is negligible

II. Probes

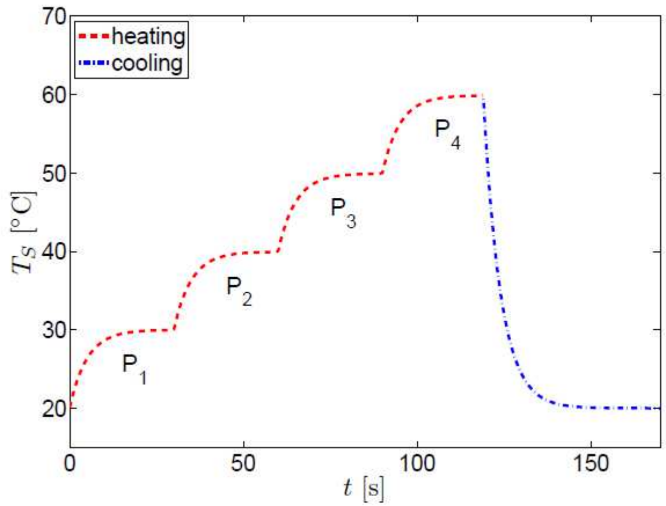
Calorimetric probes: other versions

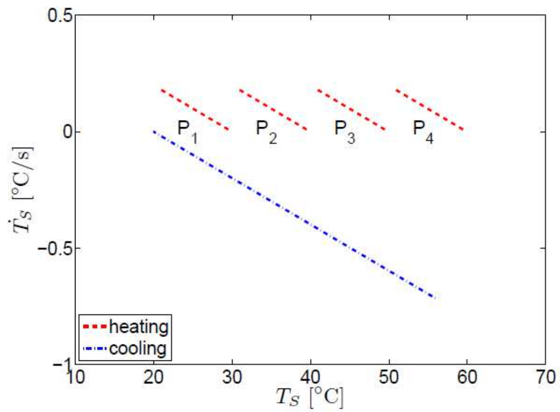
1) Transient probe

Time variation of a plasma parameter (Vb) allows continuous measurements with a calorimetric probe



S. Bornholdt et al (Eur. Phys. J. D. 67 (2013) 176)





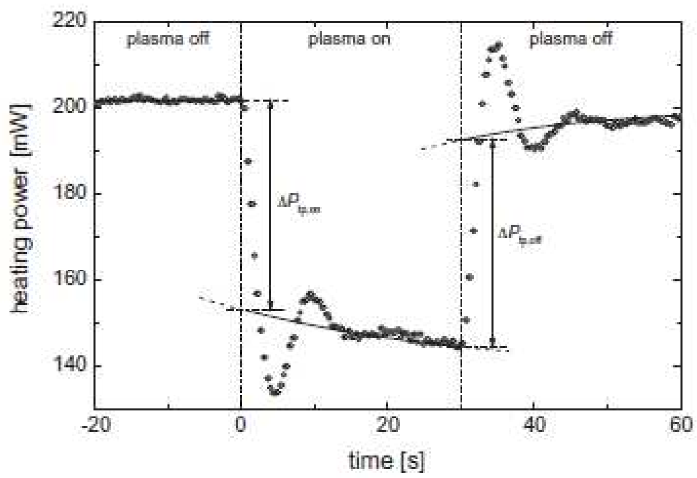
Kind of time resolution

II. Probes

2) Active probe

A probe is continously heated, its temperature is regulated (feedback loop)

The decrease of the input heating power when the plasma is lighted on is due to the energy transferred to the probe



F. May et al (Minerals Engineering 50-51 (2013) 48)

Advantages:
Direct measurement
<u>No calibration is needed</u>
Better time resolution (10s)

Drawbacks:
Difficulty to choose the « good » temperature
Problem in reactive conditions

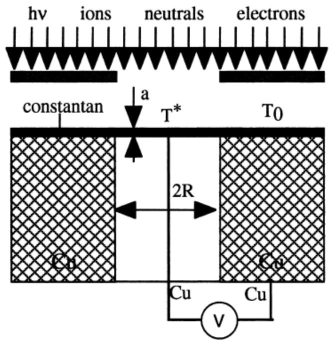
II. Probes

Probes for direct energy flux measurement

Gardon sensor

Radial ΔT between two thermoelements is followed
Temperature of one metal (Cu) is fixed

- *Detected signal directly proportional to the power flux*
- *Fast time response (< 1s)*
- *Calibration is required*



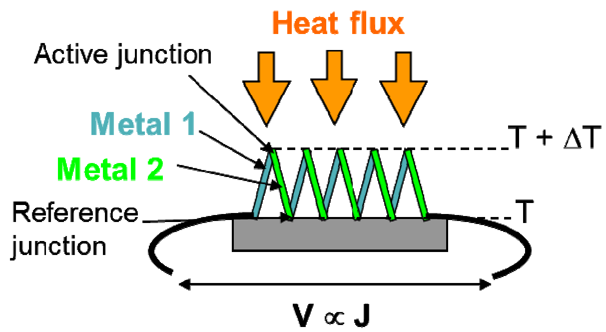
Gardon sensor *(R. Gardon 1953, K. Ellmer 1999 etc.)*

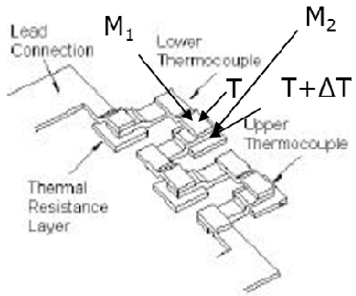
Thermopile

ΔT proportional to the power flux

1600 thermocouple junctions/cm2
sensitivity of 0,1mW/cm2

Thin film technology
fast time response: 300 µs





HFM from Vattel @

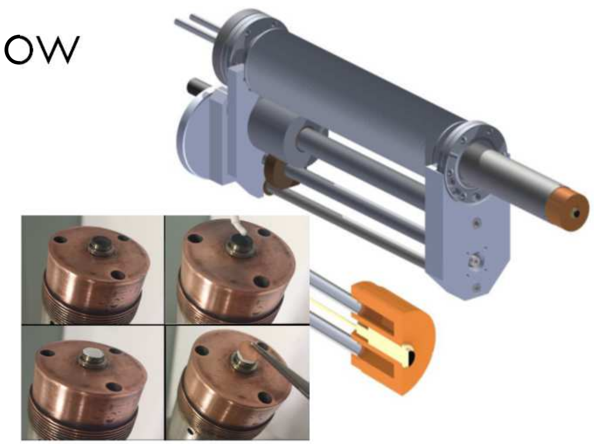
II. Probes

Energy flux diagnostic for measurements in low pressure plasmas

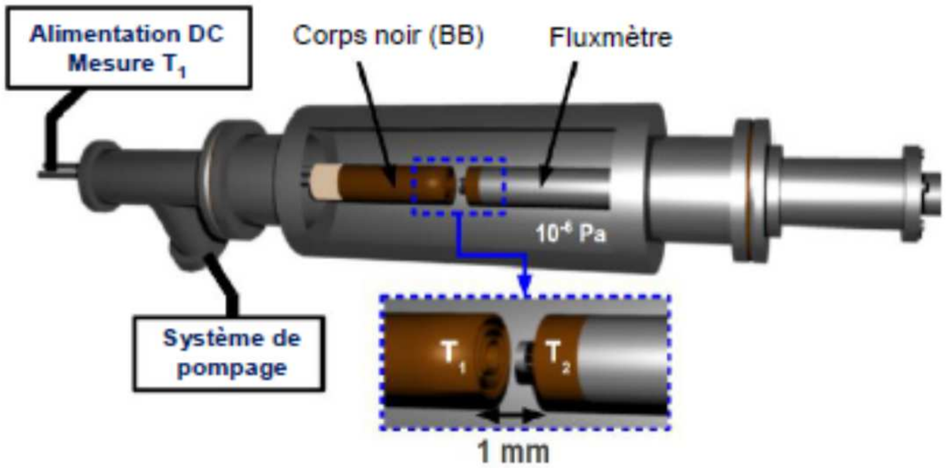
The sensor is inserted in a movable rod, cooled down to 5°C

A copper foil is pasted on the sensor

→ *degradation of the response time 300µs to 500ms*



(A.L. Thomann et al Review of Sci. Instrum. 77 (2006) 033501)



Calibration in vacuum following a NIST protocole using IR radiation from a black body and the Stefan law

$$\varphi_{1\to 2} = \sigma f_{1\to 2}(\varepsilon_1 T_1^4 - \varepsilon_2 T_2^4)$$

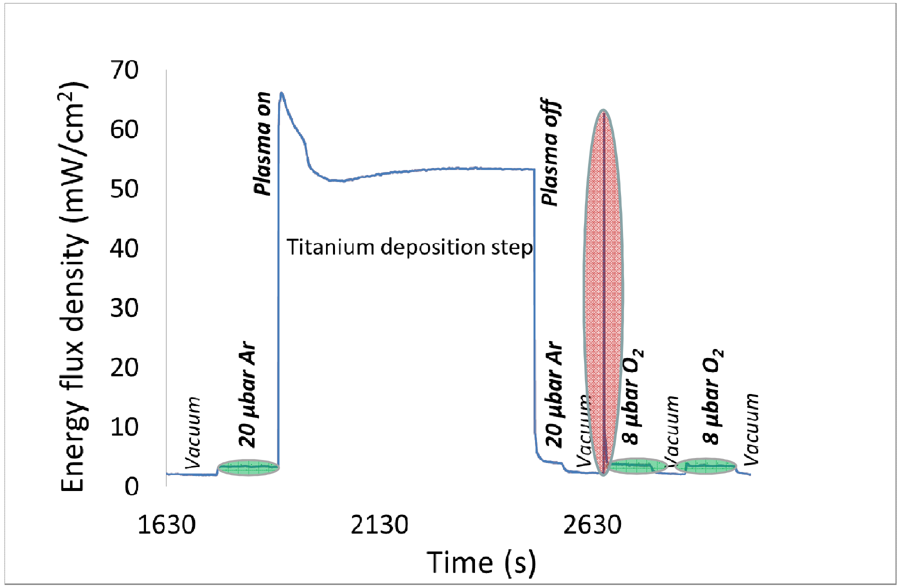
II. Probes

Example of measurements

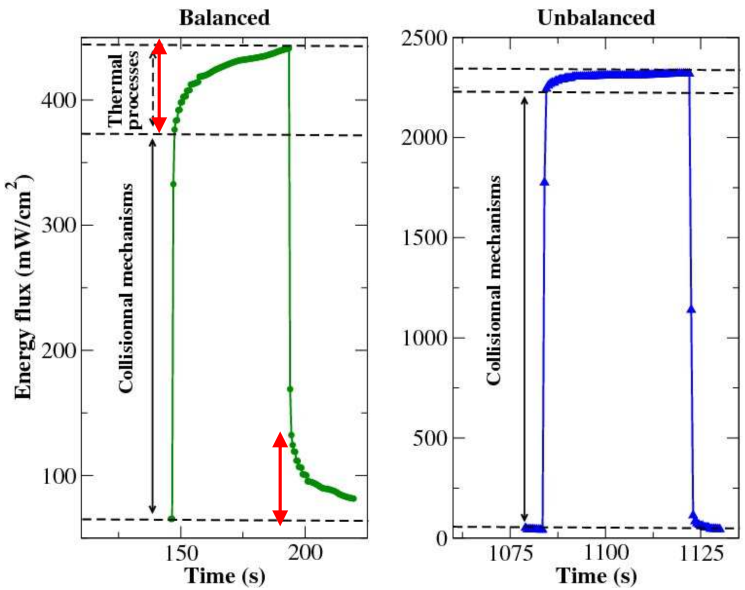
Offset: Radiatif flux between the cooled sensor and the reactor at room temperature

(Ar, O2) gas conduction

Oxidation of the Ti deposit



Ti target, 0,66 Pa, 400W

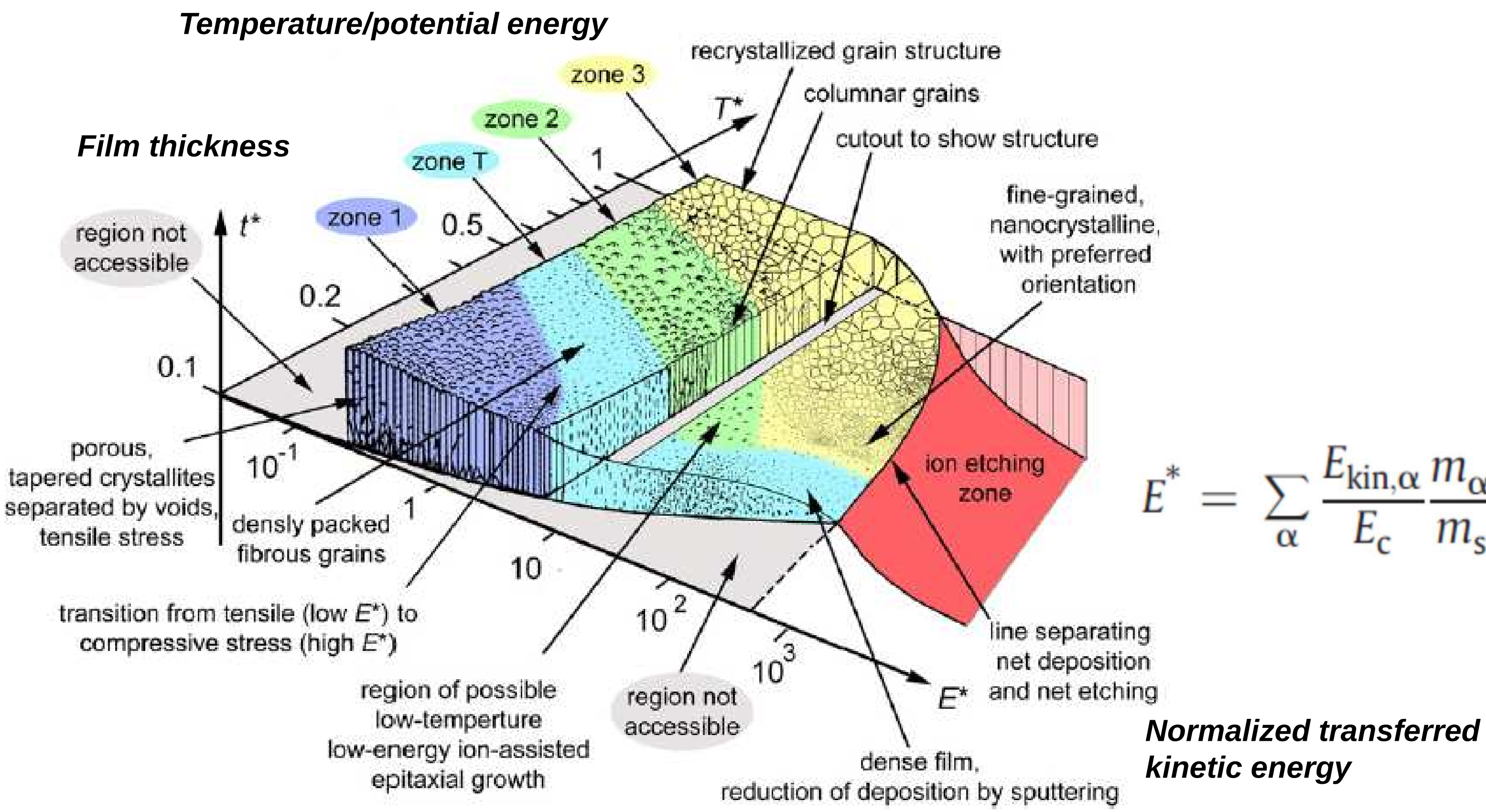


Detection of a slwo process attibuted to IR emission fromm the heated target surface

This phenomenon is furthered in the case of a balanced magnetic field

Detection and separation of various energetic contributions

III. Total energy transfer/thin film properties



$$E^{*} = \sum_{\alpha} \frac{E_{\mathrm{kin},\alpha}}{E_{c}} \frac{m_{\alpha}}{m_{s}} J_{\alpha} \Big/ \sum_{\alpha} J_{\alpha}$$

Structure zone model from Anders A.(Thin Solid Films 518 (2010) 4087–4090)

SZM: model based on the adparticle mobility that is controlled by the Etot/At

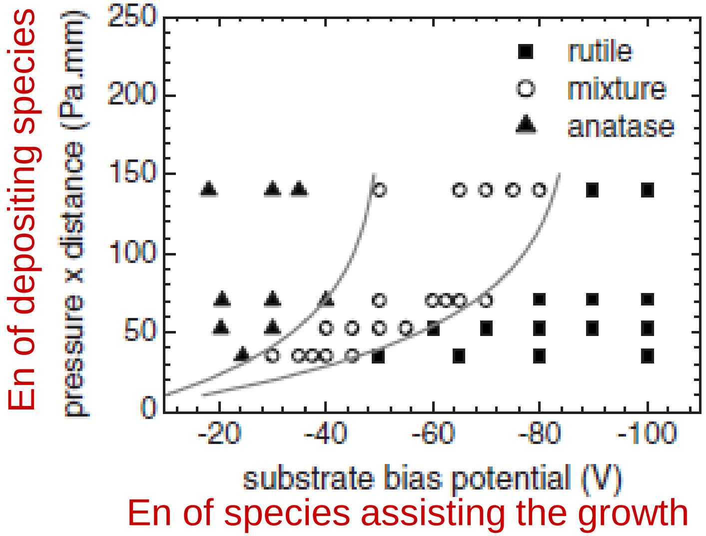
III. Total energy transfer/thin film properties

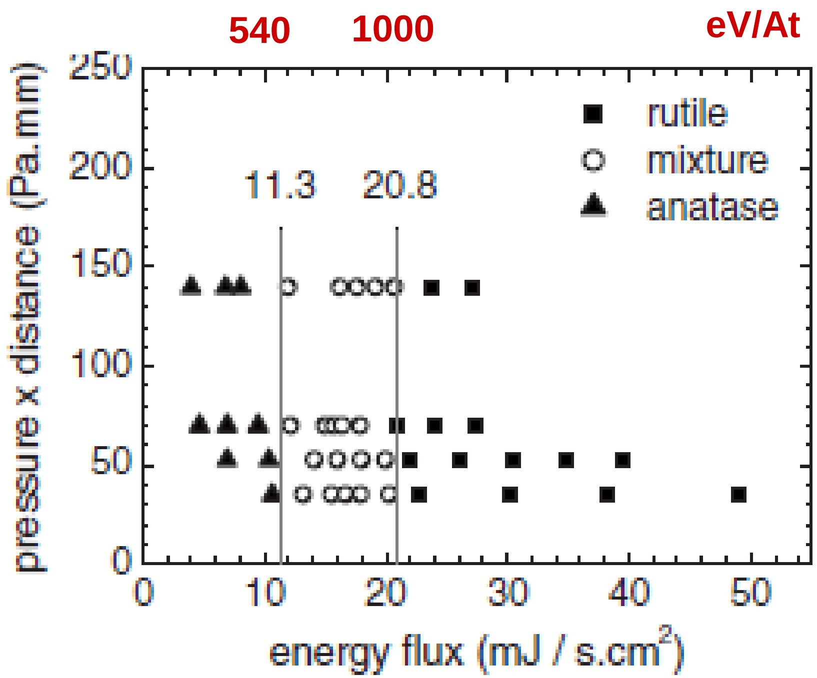
Widely investigated case of TiO_2 films

DC and RF reactive magnetron sputtering of Ti

Constant deposition rate, deposition temperature < 150°C
Constant d, various P and V_b
Ar+ ions deliver the major part of the energy

S. Mraz et al (J. Appl. Phys. 109 (2011) 023512)

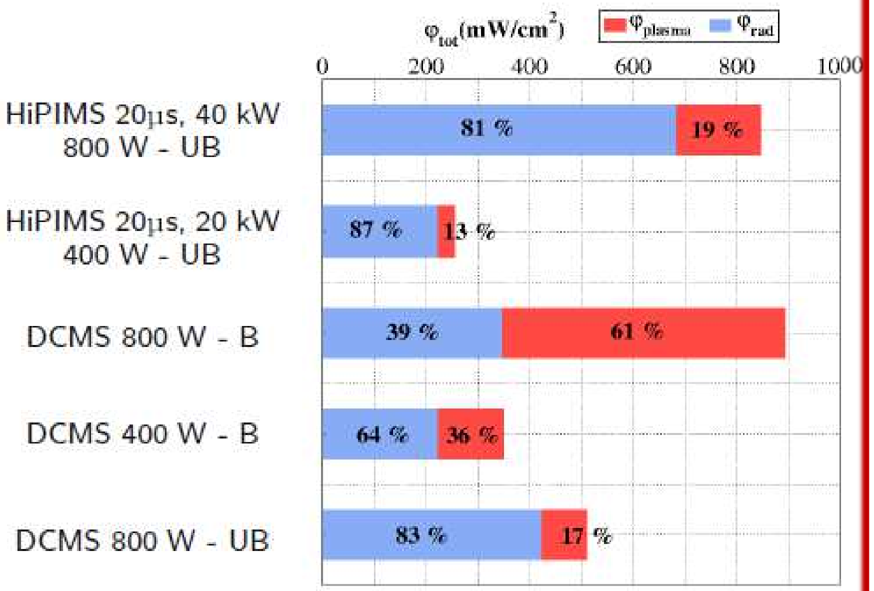




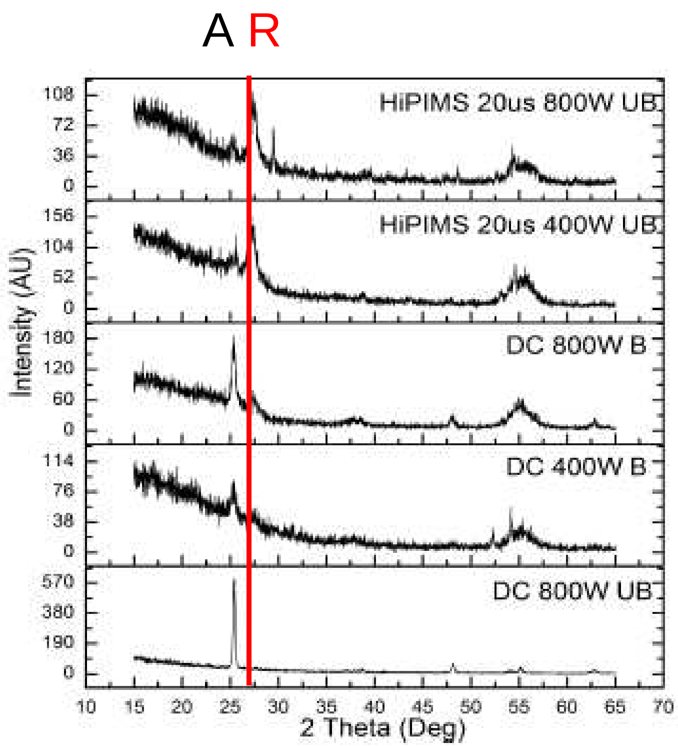
The relevant parameter is Etot/At $((J_{Ar+} \times E_{Ar+})/V_{deposition})$
(in the investigated range of deposition conditions!)

III. Total energy transfer/thin film properties

Deposition of TiO2 films in a large range of conditions



φ_N (10^3eV/At)
15,1
5,4
4,3
3,7
1,9



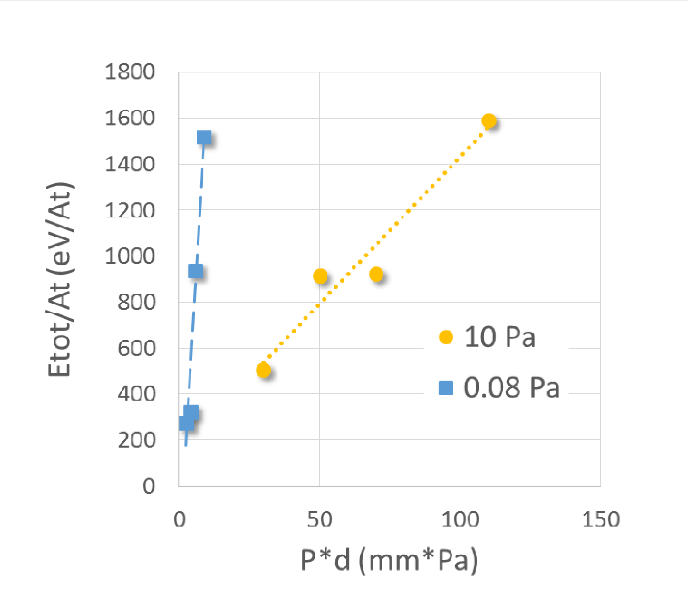
P.A. Cormier et al (Surface & Coatings Technology 254 (2014) 291–297)

En/At seems again to allow the prediction of the critalline structure

IR radiation emitted by the target has to be taken into account

III. Total energy transfer/thin film properties

Deposition of TiO2 films in a ECWR-HiPIMS system



	d = 30 mm	d = 50 mm	d = 70 mm	d = 110 mm
0.08 Pa	Rutile pref. orient. 2.7 nm/min 205 mW/cm^2	Rutile 1.3 nm/min 116 mW/cm^2	Rutile 0.5 nm/min 130 mW/cm^2	Rutile 0.3 nm/min 126 mW/cm^2
1.0 Pa	Rutile 1.6 nm/min 176 mW/cm^2	Rutile 0.9 nm/min 95 mW/cm^2	Rutile 0.5 nm/min 105 mW/cm^2	Rutile 0.2 nm/min 100 mW/cm^2
10.0 Pa	Rutile 0.9 nm/min 126 mW/cm^2	Rutile 0.3 nm/min 76 mW/cm^2	Rutile + anatase 0.2 nm/min 51 mW/cm^2	Anatase 0.1 nm/min 44 mW/cm^2

PV. Stranak et al (Surface & Coatings Technology 222 (2013) 112-117)

Data show that more than 80% of the total power flux comes from the ECWR (mainly electrons)

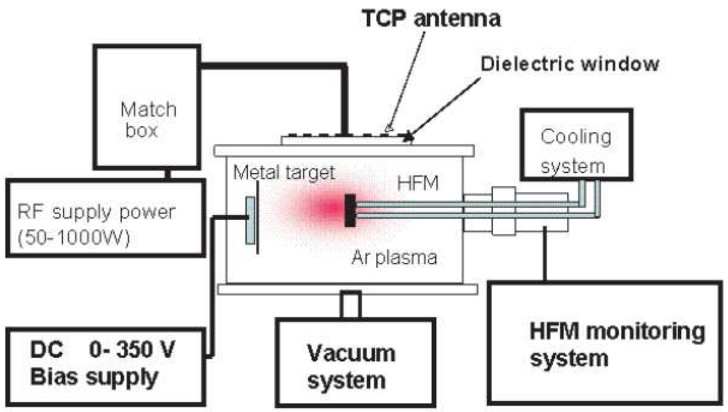
Contradictory results are found, since Anastase is formed at the highest Etot/At values !!

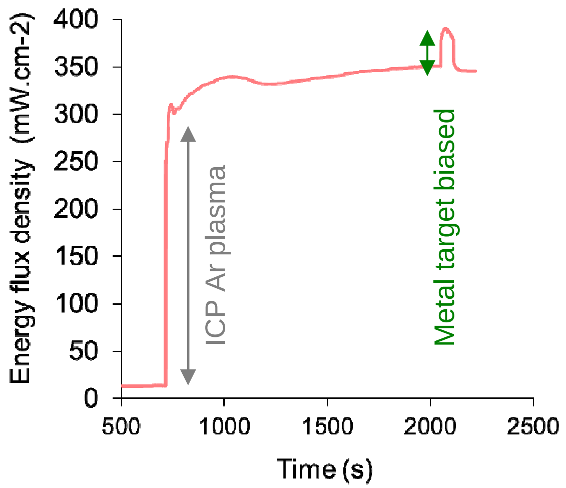
*The crystalline phase is thought to be determined by the kinetic energy of the condensing species that decreases when P*d increases*

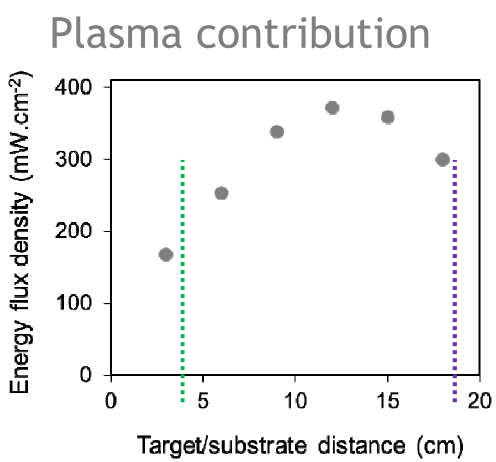
III. Total energy transfer/thin film properties

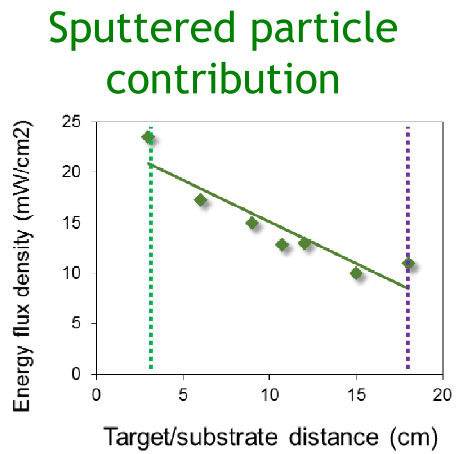
ICP Plasma sputtering of metals

In this sputtering system, plasma and sputtered species energetic contributions are uncorralated.









Samples	Pt atom number (RBS) (at/cm2)	Thickness calculated from RBS (nm)	Thickness measured on SEM images (nm)
30min, 18cm	1.1×10^{17}	17	31
11min30s, 3cm	8.5×10^{17}	128	130

17 eV/At

2 eV/At

The densest film is obtained when sputtered atom contribution is the highest, whereas the En/At is the lowest !

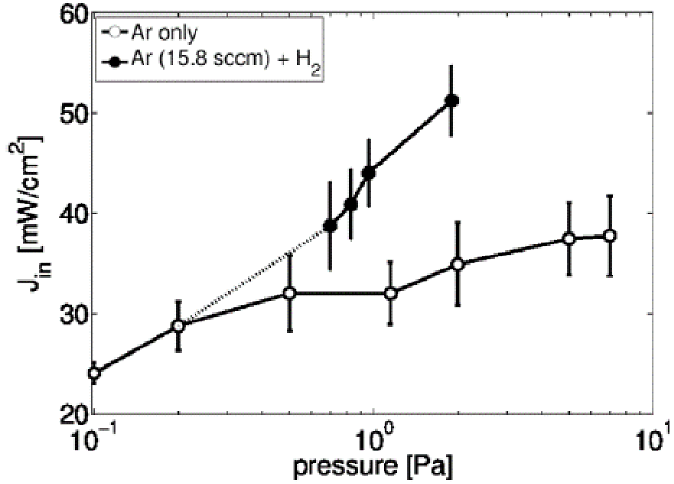
IV. Detection of chemical reactions in the film

Highlighting of chemical reaction at the growing film is not an easy task

Magnetron sputter deposition fo ZnO films

Measurement of the energy influx with a calorimetric probe with or without H_2 in the gas phase

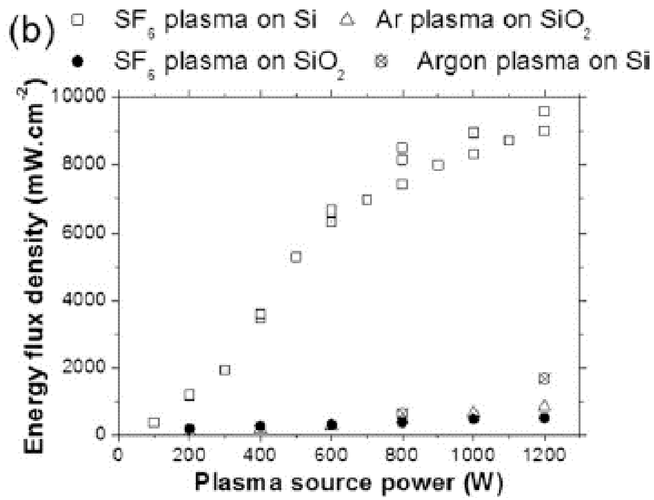
Evidence of substrate heating by the energy released when H_2 molecule is formed at the substrate



S. Bornholdt et al (Plasma sources Sic. Technol. 22 (2013) 025019

Measurements with a thermopile in ecthing and non-etching plasmas

Clear evidence fo the energy released by the formation of SiF_4 volatile molecule

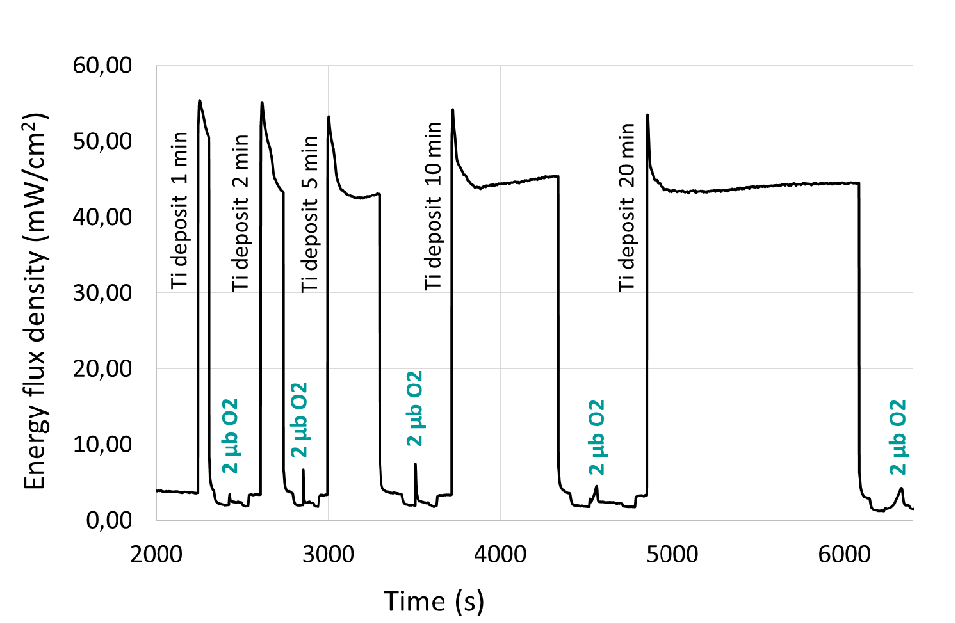


R. Dussart et al (Appl. Phys. Lett.. 93 (2008) 131502

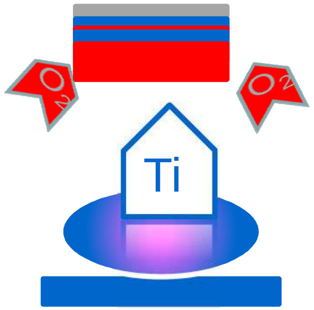
IV. Detection of chemical reactions in the film

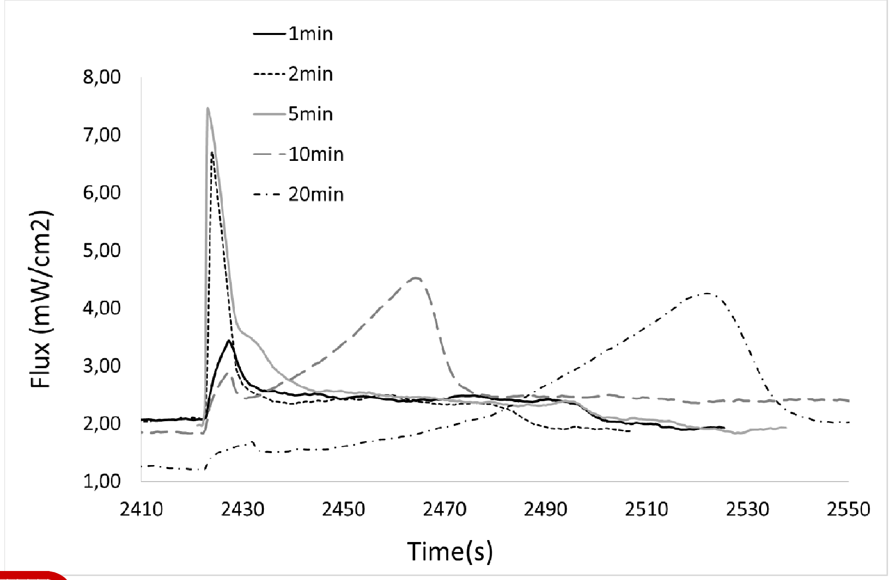
Kinetic of the energy transfer

Oxidation of Ti films with increasing thickness



Energy diagnostic





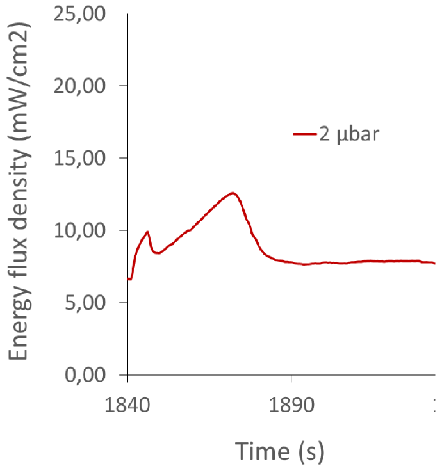
Ability to study the kinetic of the energy transferred by the chemical reaction

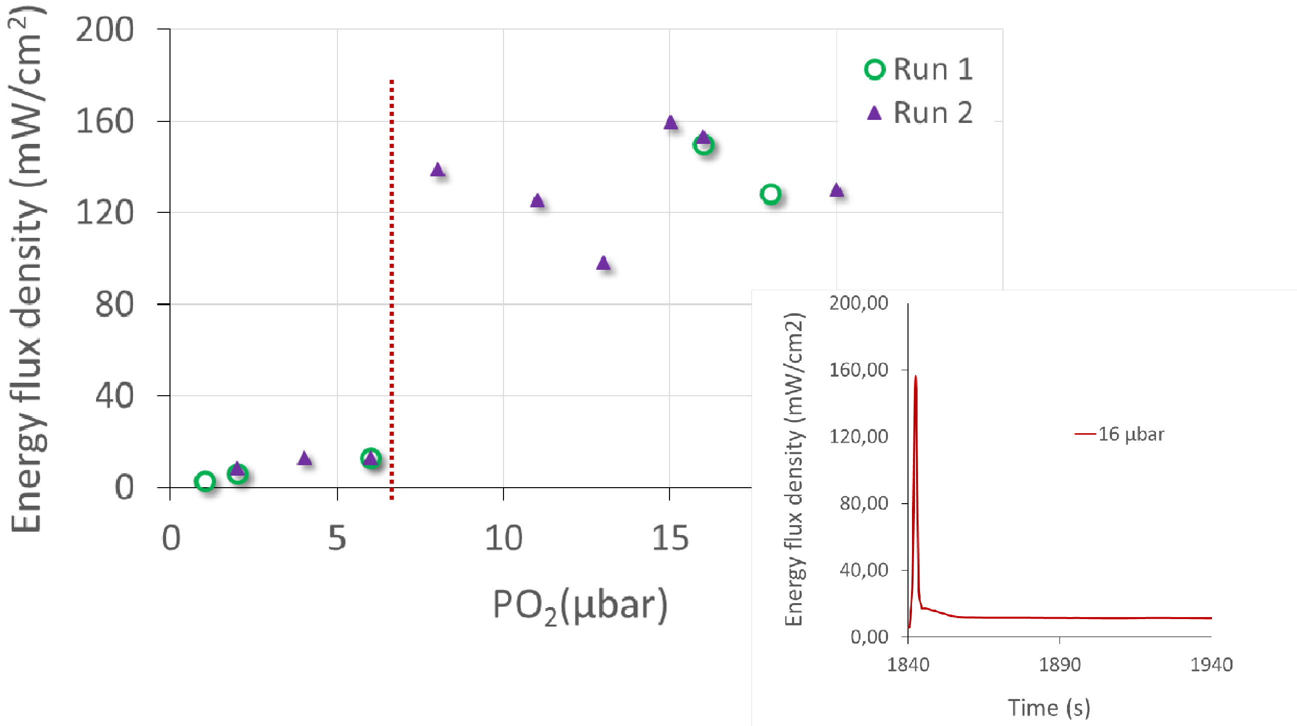
R. Dussart et al (Appl. Phys. Lett.. 93 (2008) 131502

IV. Detection of chemical reactions in the film

Kinetic of the energy transfer

Oxidation of Ti films at different oxygen pressures (different P_{O2}/At_{Ti})





Two regimes of oxidation and/or type of oxide

IV. Detection of chemical reactions in the film

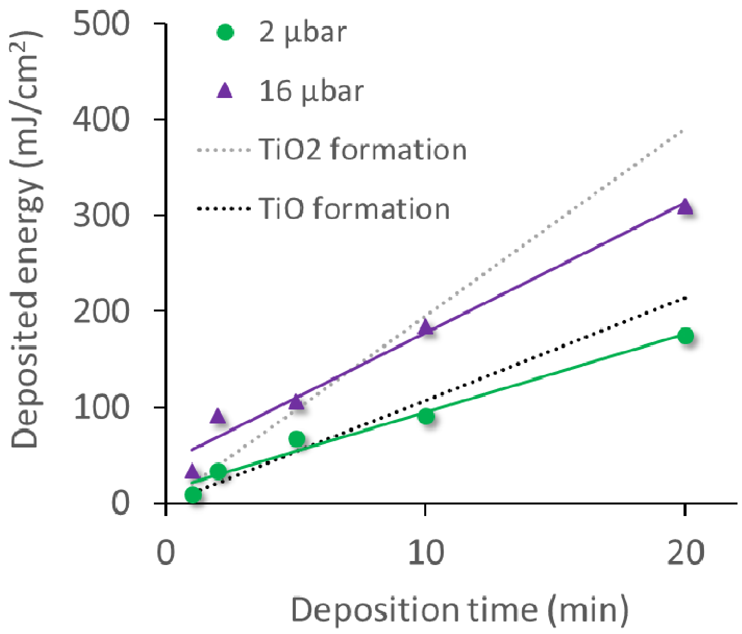
Amount of energy released by the oxidation of Ti film

$$F_{ox} = \Delta H_{ox} \times N_{Ti} \qquad N_{Ti} = \frac{d_{Ti} * H}{M_{Ti}}$$

d_{Ti}: *Ti density*

H : *thickness of the deposited Ti film*

M_{Ti} : *molar mass*



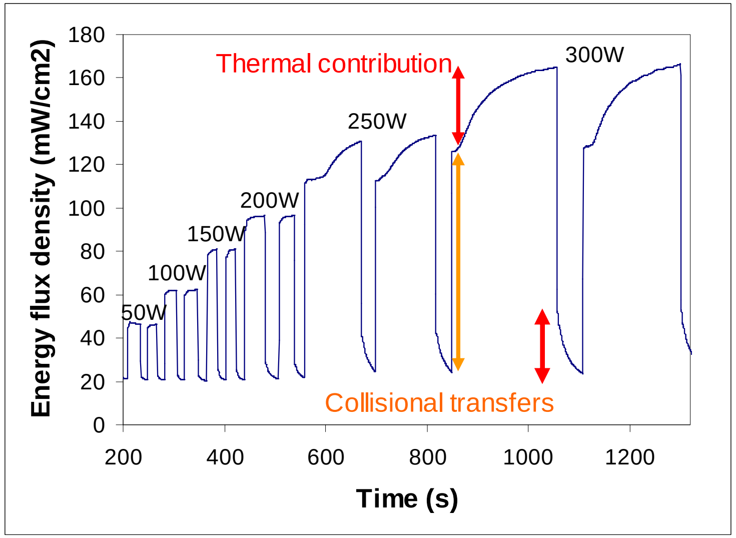
The whole Ti deposit is oxidized but the oxide formed is different, depending on PO_2

The amount and kinetics of the energy deposited is a kind of fingerprint of the process that takes place

Those processes take place during reactive magnetron sputtering depending on the oxygen residual pressure (metal regime) … Not so easy to evidence among the other contributions !

V. IR radiation contribution

Detection of a IR contribution coming from the heated target surface



A part of the input power is lost for the sputtering process

Ability to estimate T_t from the Stefan law

$$\varphi_{rad} = f_{Met/Cu}\,\sigma\left(\varepsilon_{Met}T_{Met}^{4} - \varepsilon_{Cu}T_{Cu}^{4}\right)$$

First phase transition of de Ti target is α-Ti ➙ β-Ti at 882 °C

This IR contribution can be ignored…

…whereas it could influence the growth mode

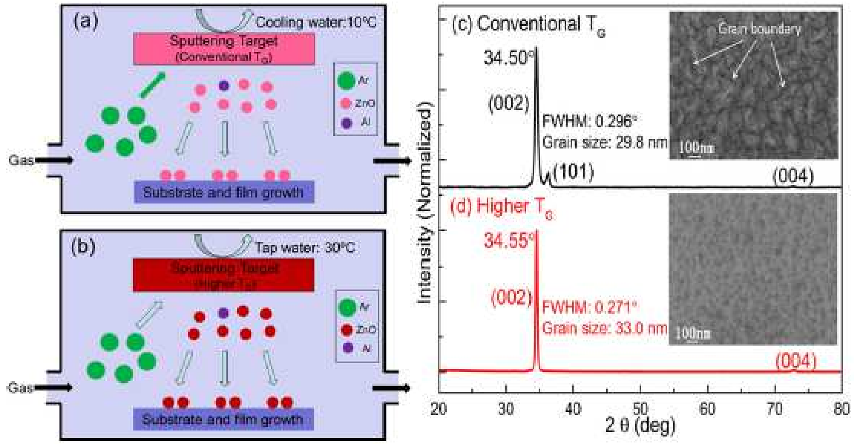
Power (W)	Plasma contribution (mW/cm2)	IR contribution (mW/cm2)	Percentage of IR emission	τ (s)	Target surface temperature (°C)
100	124	14	9.5 %	7	211
200	191	23	10.3 %	8	269
400	315	45	12.2 %	6	362
800	562	148	20 %	9	577

V. IR radiation contribution

Al-doped ZnO deposited by RF magnetron sputtering

Limitation of the cooling efficiency to allow the targer surface temperature to rise

Self-heating of the target promotes the crystalline quality od the film



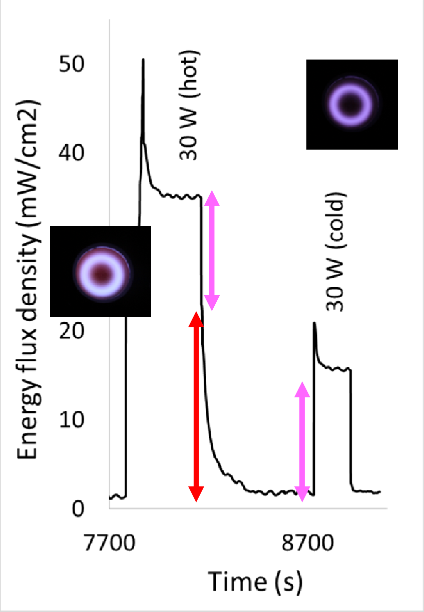
W. F. Yang et al (Appl. Phys. Letters 102 (2013) 111901

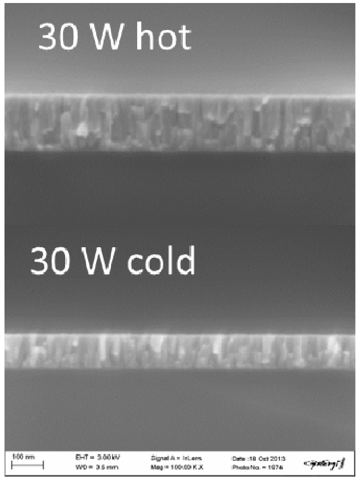
Deposition of Ni films with a « hot » target

Clear evidence of IR contribution in « hot » target configuration

20% higher deposition rate

A. Caillard et al (IEEE transition on plasma science 42(10) (2014) 2802





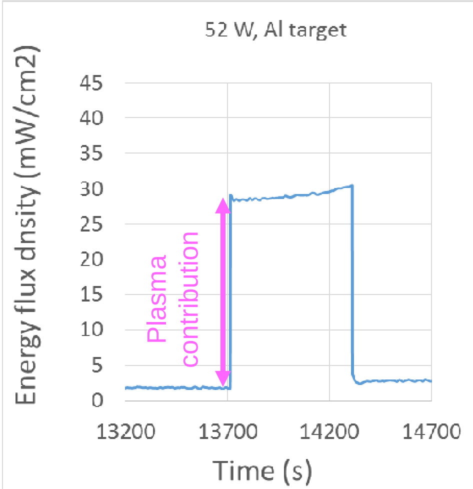
V. IR radiation contribution

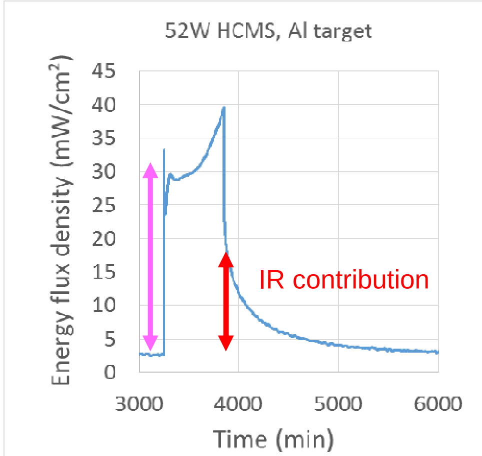
Al magnetron sputtering in « hot » target configuration

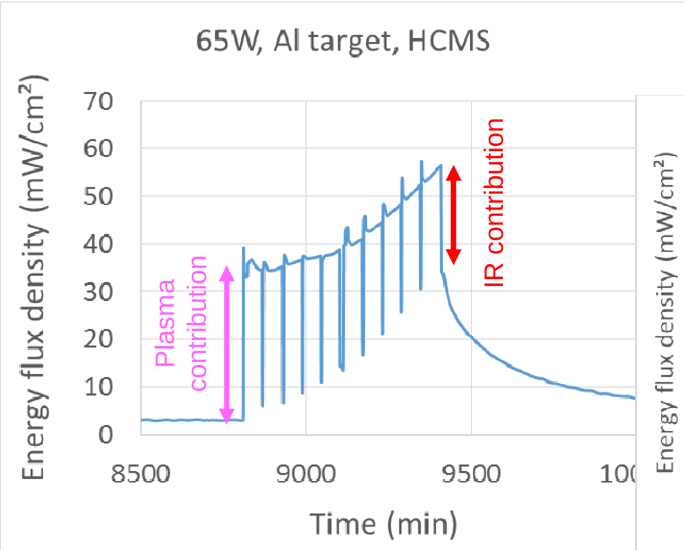
Thermal disconnection keeps the plasma contribution unchanged while the IR emission rises:

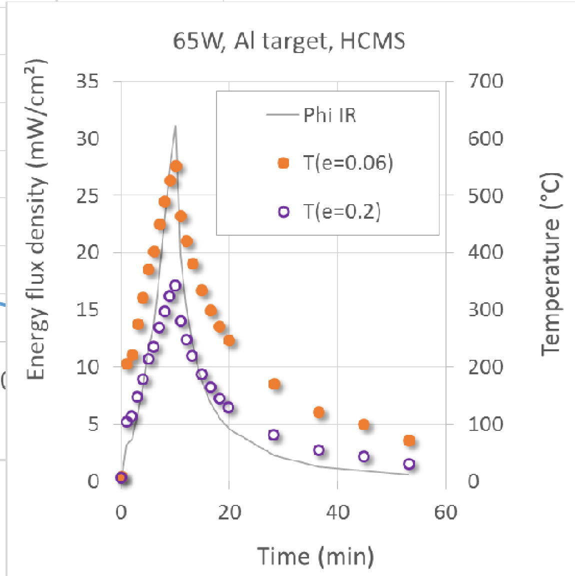
$\Delta\Phi_{plasma}$ = *28 mW/cm²*

$\Delta\Phi_{IR}$ = *0 to 17 mW/cm²*









Ability to follow the target temperature increase and to control the process close to the melting point

Knowledge of the average emissivity is of particular importance !

Conclusion

Great interest of studying energy transfers at the substrate during magnetron sputter deposition

- Total energy deposited / condensing atoms is not an universal parameter
- With fast response time sensors:
  - ability to decorralate energetic contributions of different kinetics
  - detection of IR emission from the target:

    indirect information on the target temperature and state
  - real time control of the sputtering/deposition process
- With high sensitivity sensors:
  - detection of low intensity contributions such as chemical reactions

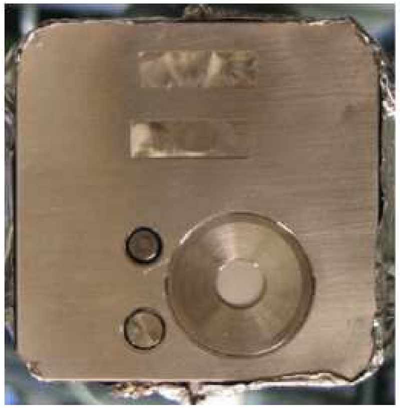
Conclusion

Correlation with conventional plasma/material analysis techniques:

Ability to evidence mechanisms taking place during sputtering and film growth processes…

…because deposited energy is a fingerprint of involved elementary mechanisms

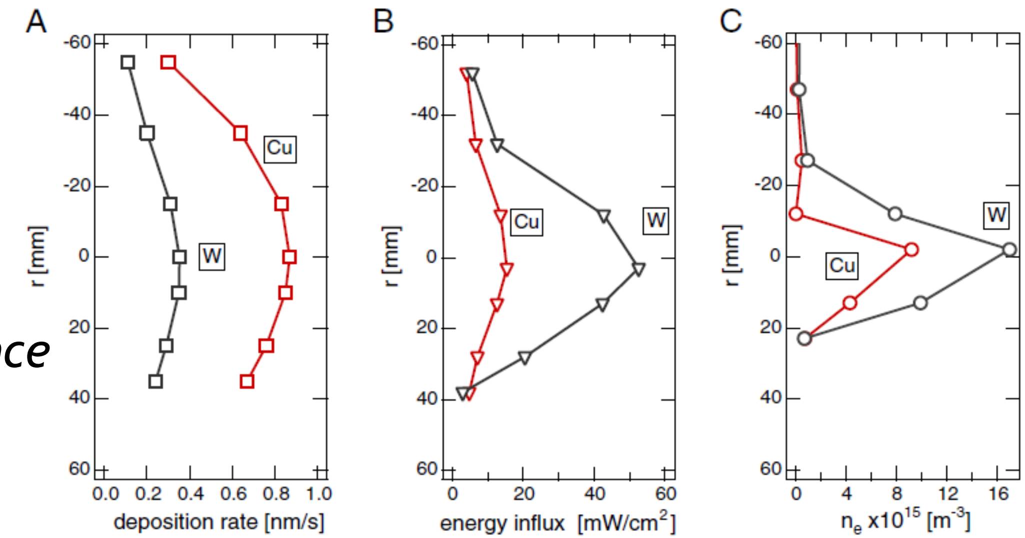
Interest of Combined sensor



Gardon probe

Langmuir probe

Quartz microbalance



K. Harbauer et al., TSF 520, 6429 (2012)

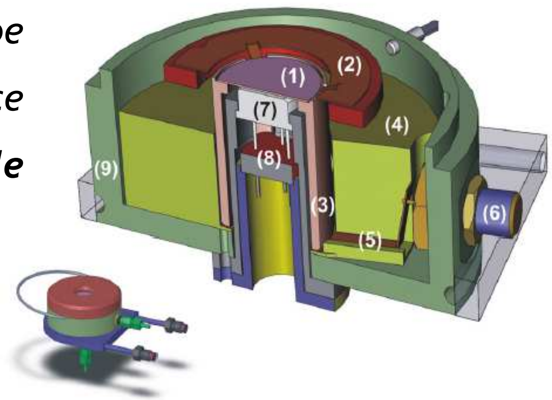
Conclusion

Interest of Combined sensor

Langmuir probe

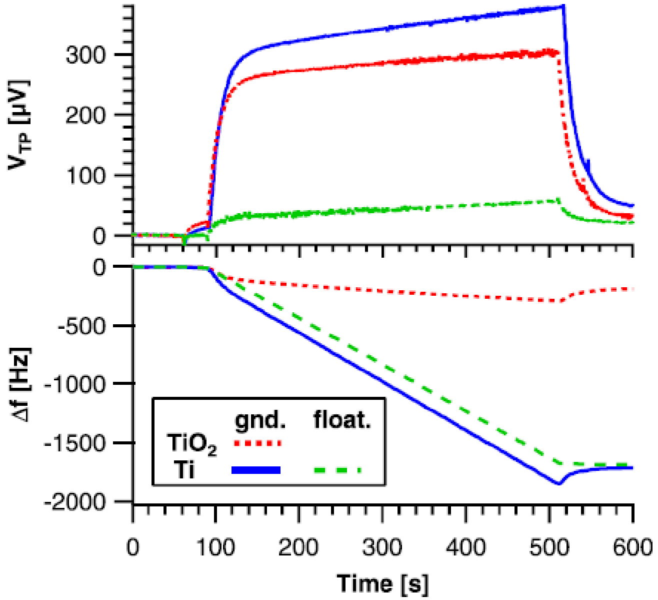
Quartz microbalance

Thermopile

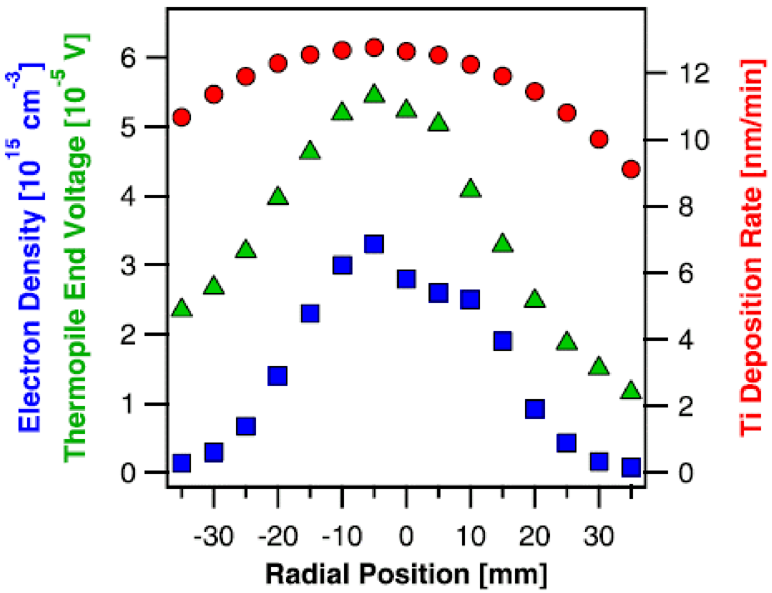


TiO2 (50%of O2) / Ti deposition:

Very lower deposition rate for a similar deposited power density : (oxidation) or high energetic species in oxide regime



T. Welzel et al., Appl. Phys. Letters 102 (2013) 211605



Charged particles and neutrals contribute to the energy transfer

Thank you !!

Amer MELHEM

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