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Ionenverteilungen beim Magnetronsputtern verschiedener Metalle in Argon/Sauerstoff

XVII. Erfahrungsaustausch "Oberflächentechnologie mit Plasma- und Ionenstrahlprozessen“
Mühlleithen, 2. – 4. März 2010

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Introduction

- one of the main advantages of magnetron sputtering:

  assistance of the film formation by energetic particles

  $\rightarrow$ neutrals from the sputtering process
  $\rightarrow$ electrons from the plasma
  $\rightarrow$ **ions (positive and negative)**
  $\rightarrow$ radicals

  } high energies due to electric fields (electrons and ions)

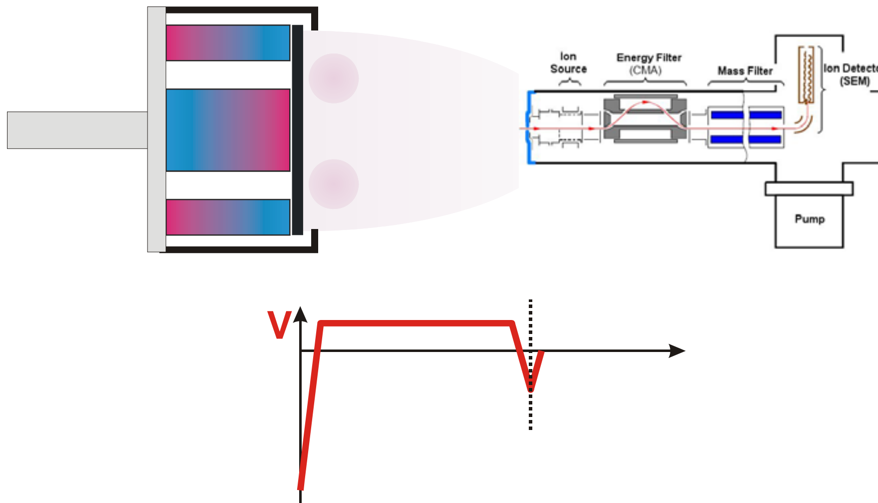
- compound formation by admixture of reactive gas component (**O_2**, N_2, CH_4, H_2S, ...)

  $\Rightarrow$ reactive mode ... particularly high (negative) ion energies

These ion energies may in some cases (e.g. microelectronics, photovoltaics) be too high and detrimental causing radiation damage in the films.
Adjustment/suppression needs knowledge of ion formation mechanisms and energies.

Measurement of Ion Distributions

schematic representation of the measurement setup



mass spectrometer: plasma process monitor PPM 422 (Inficon)

- in place of substrate holder
- 60 mm distance from target
- energy range: 0 ... ± 500 eV
- mass range: 0 ... 500 amu
- entrance orifice (Ø = 1 mm) at floating potential

- **acceptance angle of few degrees: ⇒ only perpendicular incidence**

sputter setup: circular planar magnetron (∅ = 50 mm), d.c. discharge, P = 50 W

- different target materials: Mg, Cu, In, W
- working gas: 100 % Ar (non-reactive)
  50 % Ar + 50 % O_2 (reactive)
- working gas pressure: 0.5 Pa ... 1.7 Pa

Target Voltages in Ar and Ar/O_2

	0.9 Pa, 50 W const. power			*Depla et al., JAP 101 (2007) 013301 const. current*		
	U_{met} [V]	U_{ox} [V]	U_{ox}/U_{met}	γ_{met}	U_{ox}/U_{met}	γ_{ox}
Mg	**276 ± 2**	**155 ± 1**	0.56	*0.14*	*0.47*	*0.41*
Cu	**281 ± 1**	**325 ± 3**	1.2	*0.082*	*1.04*	*0.071*
In	**397 ± 9**	**395 ± 9**	0.99	*0.10*		*0.092*
W	**246 ± 12**	**418 ± 6**	1.7	0.10		< 0.08

tungsten: according to $U_{ox}/U_{met} \Rightarrow \gamma_{ox}/\gamma_{met}$ much lower than for Cu (0.87)

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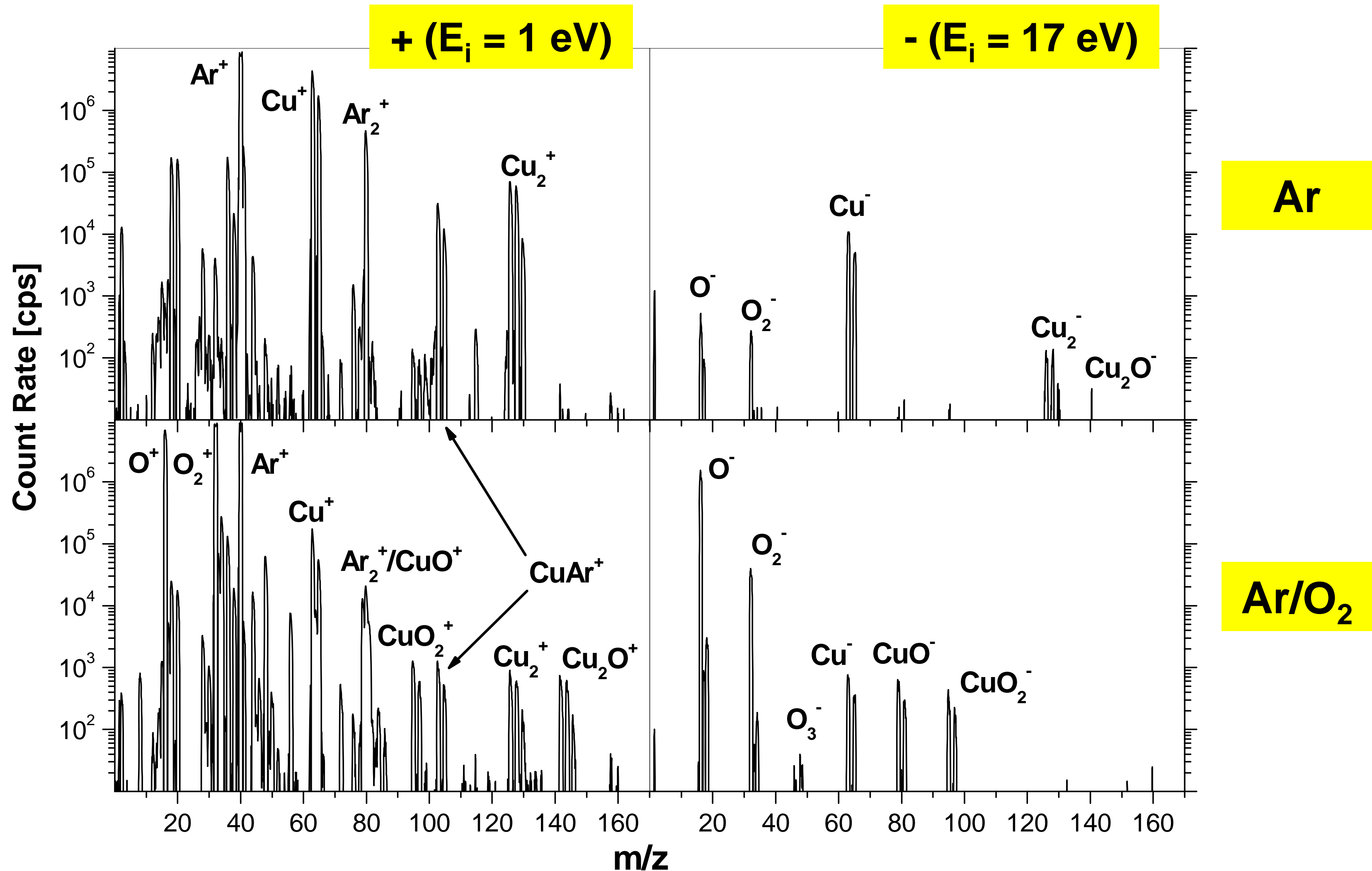
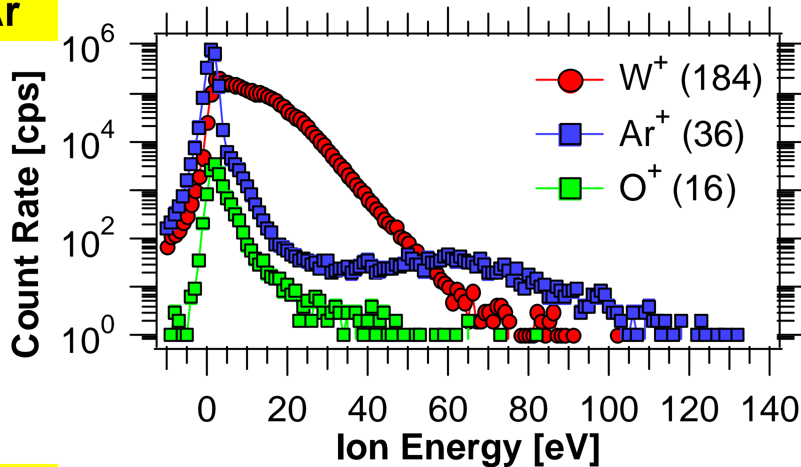
Mass Spectra with Cu Target

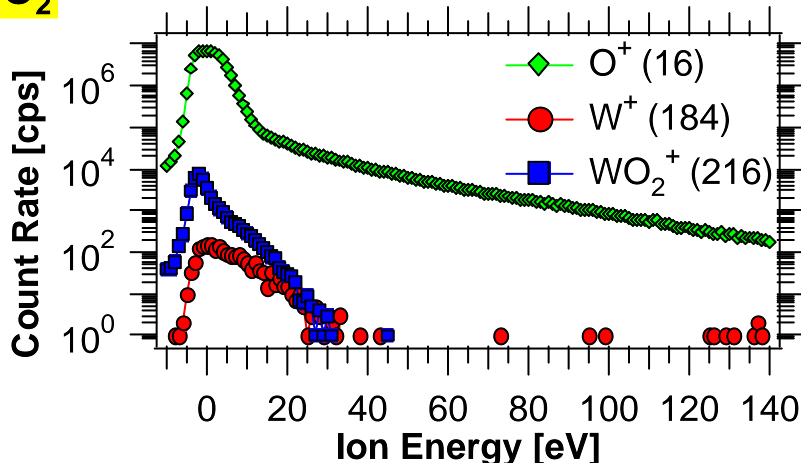


Positive Ion Distributions: Typical Spectra

Ar



Ar/O_2



general:
- peak at low energy (~eV_{pl})
- high-energy tail (sputter distribution)
- additional Ar^+ @ 50 ... 100 eV

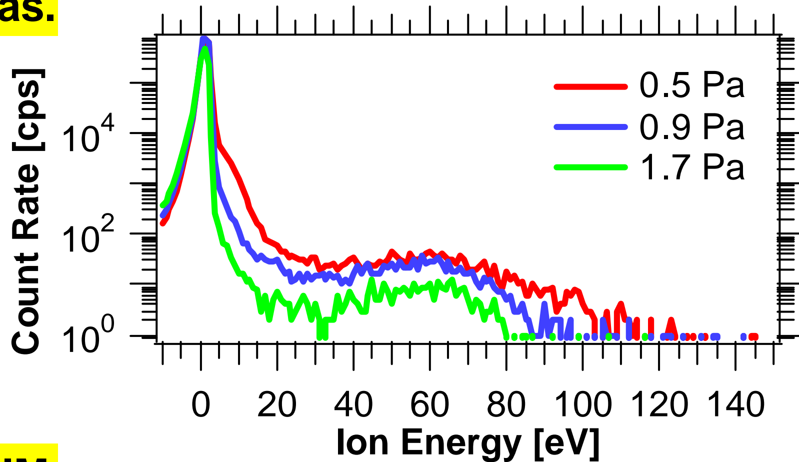
non-reactive (Ar):
- mainly M^+ and Ar^+
- impurity signals of O^+ (MO_x^+)

reactive (Ar/O_2):
- mainly Ar^+, O^+, and O_2^+
- O^+ extended to very high energy
- weak M^+ (reduced sputter yield)
- different molecules $M_{(y)}O_x^+$

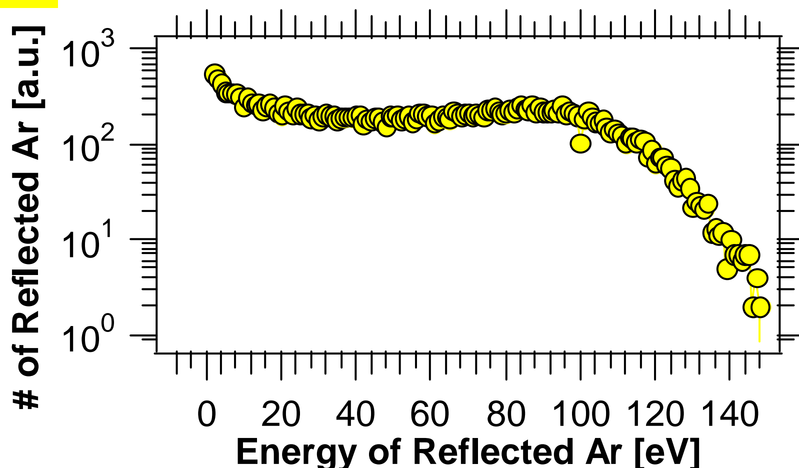
W target , P = 50 W, p = 0.5 Pa, centre, 6 cm distance

Positive Ion Distributions: High-Energetic Working Gas (Ar^+)

Meas.



TRIM



broad maximum/extension at energies of several 10 eV to (some) 100 eV:

⇒ dependent on target mass (not for Cu, Mg)

⇒ dependent on gas phase collisions

⇒ gas heating or **projectile reflection**

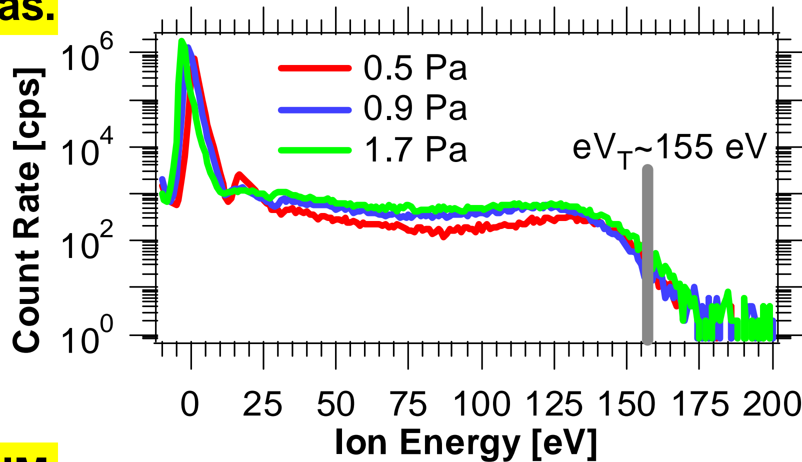
TRIM simulations (Ar^+ (256 eV) → W):

- similar distribution
- slightly higher energy (no collisions)
- only for heavy targets

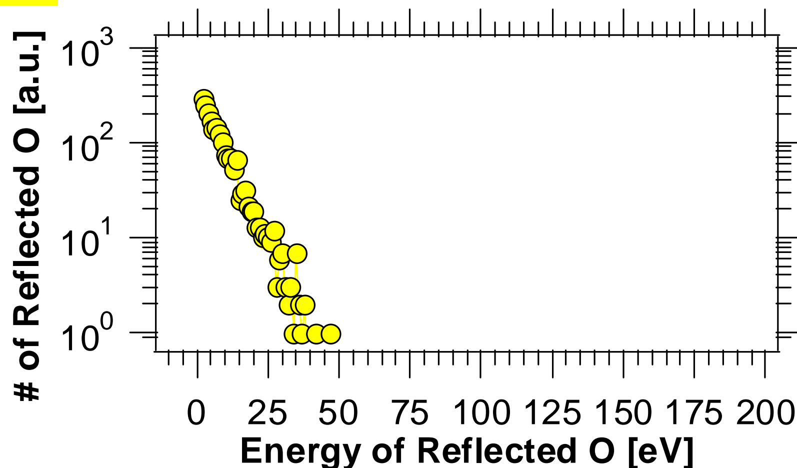
W target , P = 50 W, Ar, centre, 6 cm distance

Positive Ion Distributions: High-Energetic Working Gas (O^+)

Meas.



TRIM



broad maximum/extension to energies far above 100 eV:

⇒ observed for every target material

MgO:

⇒ low discharge voltage (~155 V)

⇒ signal extents to full voltage equivalent

TRIM simulations (O^+ (158 eV) → MgO):

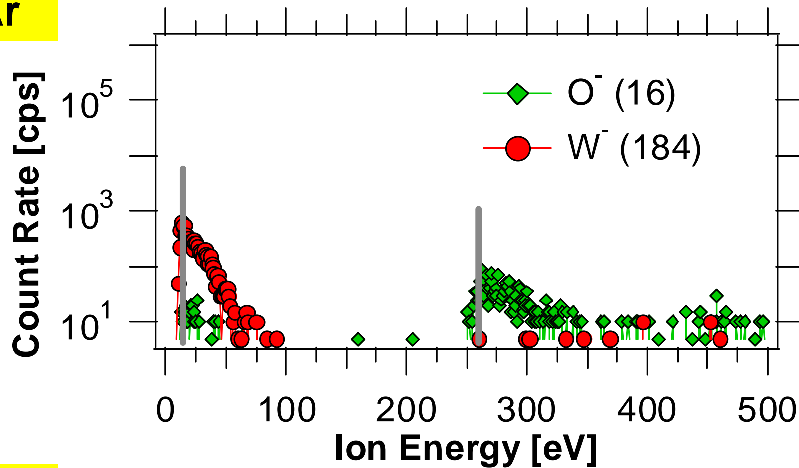
⇒ energy of reflected O much too low

⇒ In contrast to Ar^+ (reflection + post-ionisation), high-energetic O^+ is not due to reflected atoms – instead to O^-.

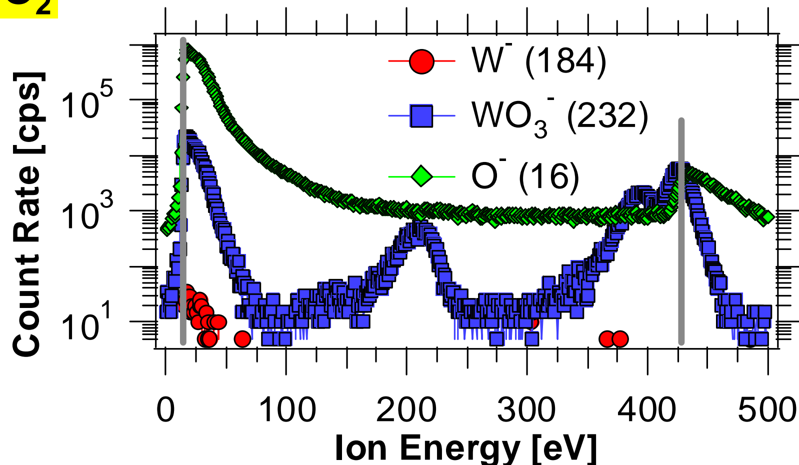
Mg target , P = 50 W, Ar/O_2, centre, 6 cm distance

Negative Ion Distributions: Typical Spectra

Ar



Ar/O_2



weak signals in <u>non-reactive</u> mode:

- metal ions, if $E_a > 0$ (W, In, Cu)
- weak impurities

more signal(s) in <u>reactive</u> mode:

- O^-, O_2^-, $M_{(y)}O_x^-$
- high-energy (several 100 eV) peak
- low-energy signal (< 100 eV)
- partially mid-energy peaks

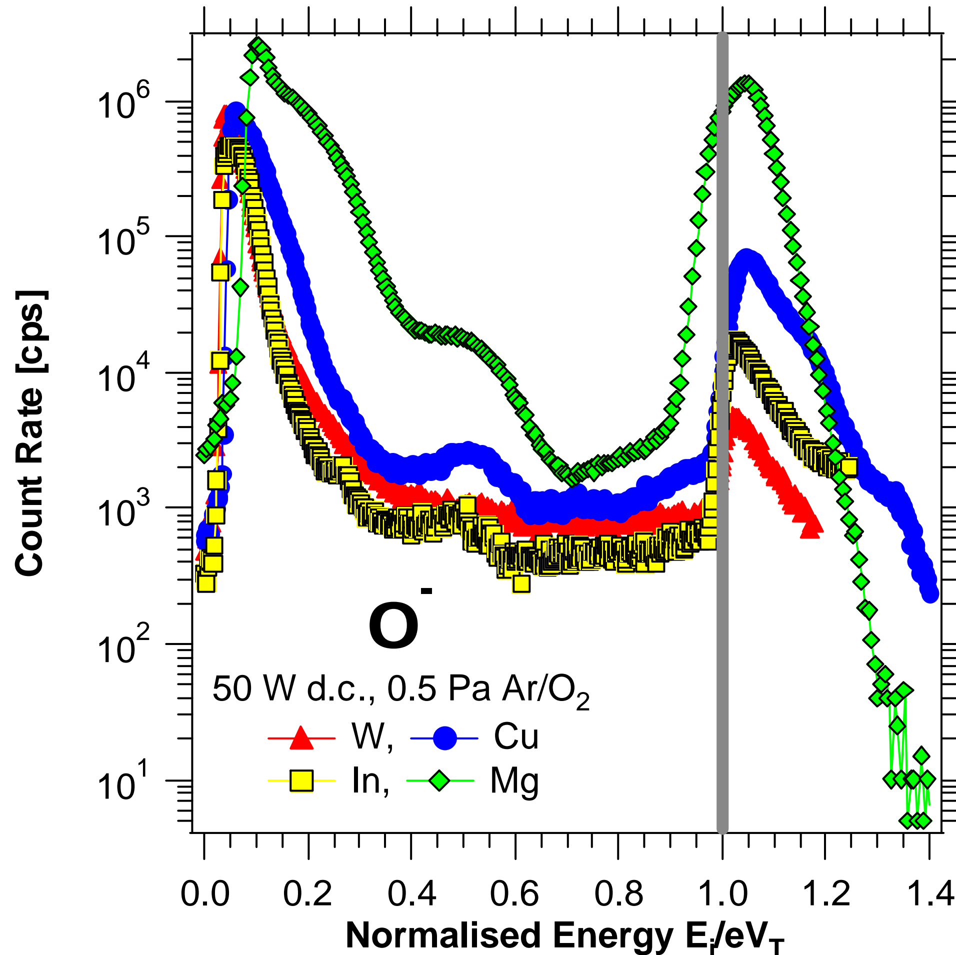
general:

- low-energy cut-off: $E_{min} = eV_{fl}$ to enter PPM

$\Rightarrow$ no detection of “cold“ ions formed from working gas

W target , P = 50 W, 0.5 Pa, centre, 6 cm distance

Negative Ion Distributions: High-Energy Peak



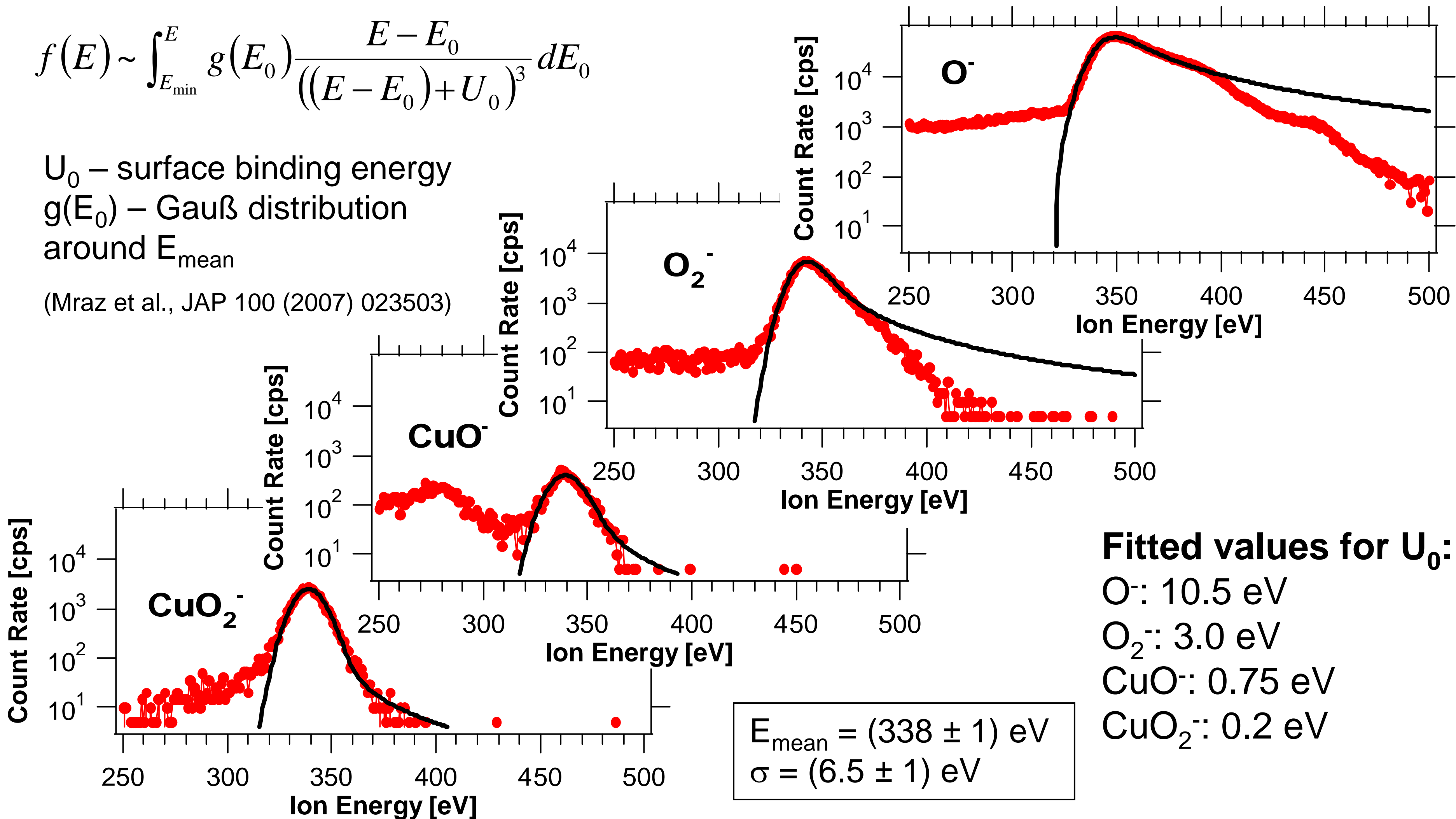
- IDF of O^- for different target materials, normalised to the respective target voltage V_T
- peak generally located at eV_T

⇒ negative O^- ions formed directly at the target surface

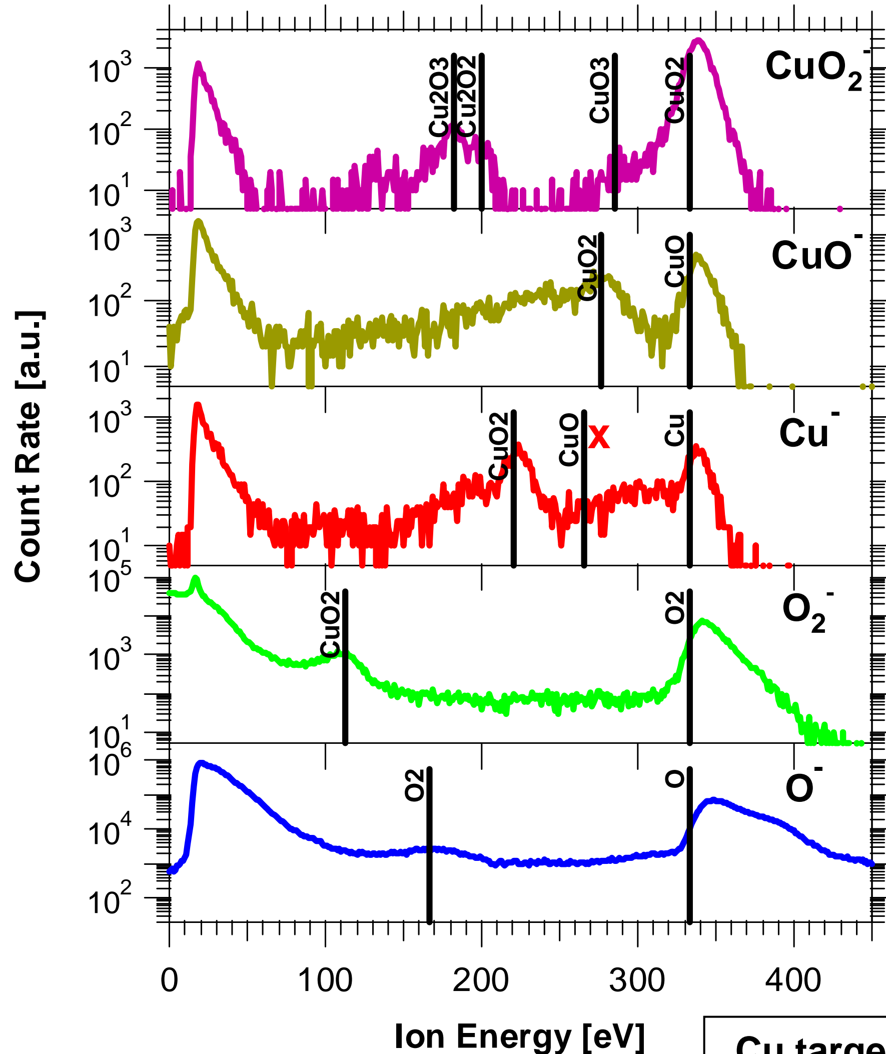
⇒ accelerated by full sheath potential

- similar for all other negative ions

Negative Ion Distributions: High-Energy Tail



Negative Ion Distributions: Mid-Energy Peaks (Cu)

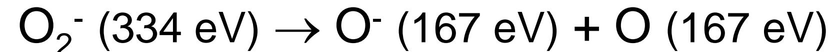


distinct peaks between eV_T and eV_{fl}:

- depend on target and detected ion

$\Rightarrow$ fragments from molecular ions formed at the target (full energy)

e.g.:



O_2^- (334 eV) $\rightarrow$ O^- (167 eV) + O (167 eV)

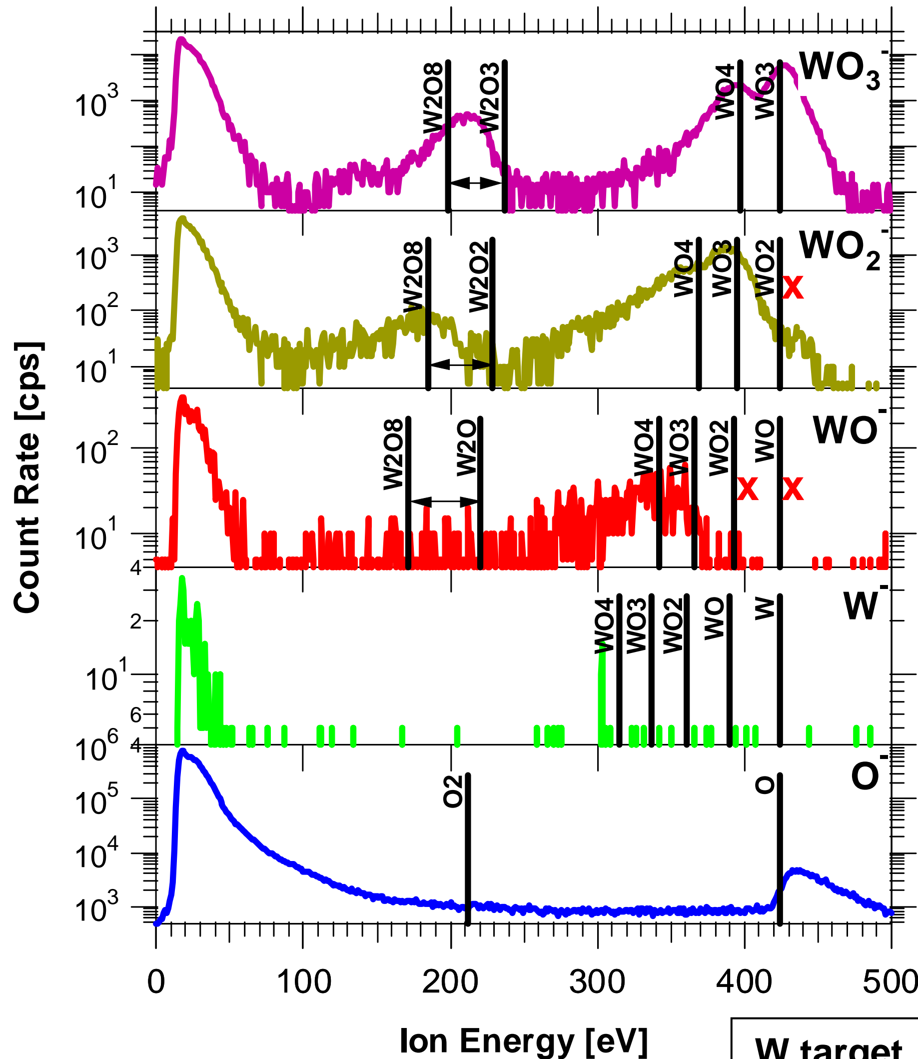
CuO_2^- (334 eV) $\rightarrow$ CuO^- (278 eV) + O (56 eV)

possible formation paths:

- spontaneous decay
- electron collision + re-attachment
- not: gas-phase collisions – scattering out of the small detection angle

Cu target, P = 50 W, 0.5 Pa Ar/O_2 = 50/50, centre, 6 cm distance

Negative Ion Distributions: Mid-Energy Peaks (W)



- parent molecules up to WO_4^- and $W_2O_x^-$ detected
- **no WO^- or WO_2^-** at full energy of fragments of them ⇒ not **formed at the target**
- dominant molecule WO_3^- (E_a > 2.5 eV, $E_a(W)$ = 0.8 eV, $E_a(O)$ = 1.5 eV)
- so far no correlation to neutral molecular abundance (signal depends on E_a)

W target , P = 50 W, 0.5 Pa Ar/O_2 = 50/50, centre, 6 cm distance

Conclusions

non-reactive sputtering:

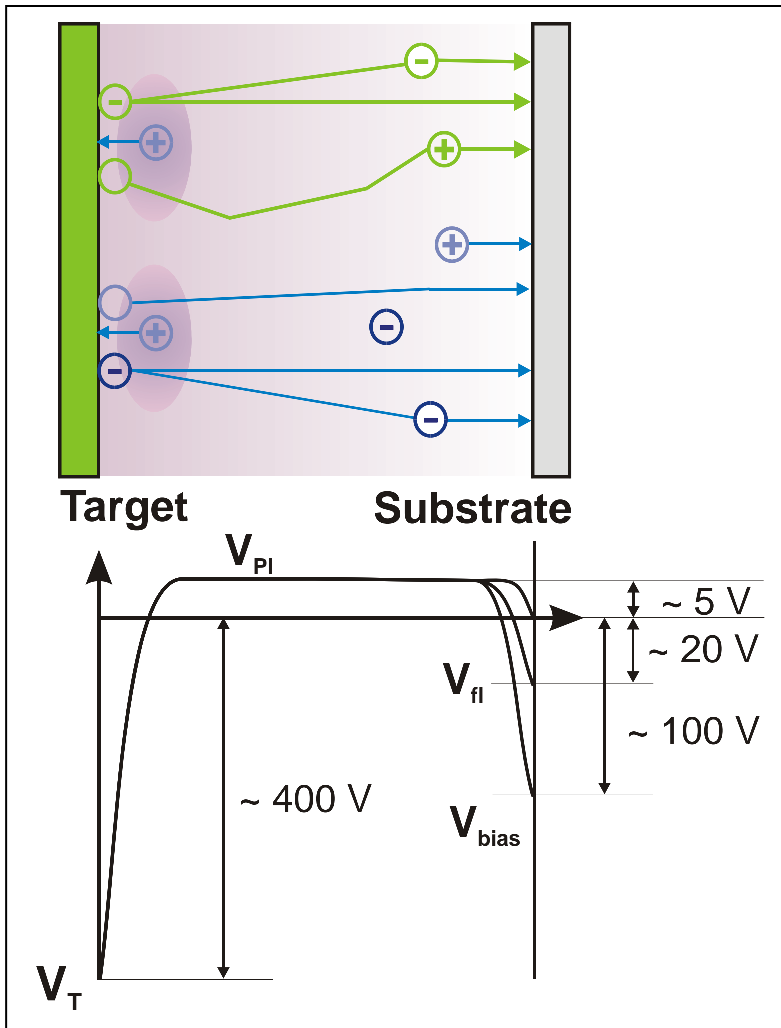
- low-energetic positive ions
- for target material ions with high-energy tail
- mid-energetic reflected gas atoms (heavy targets)
- few negative ions (electronegative metals, impurities)

reactive sputtering:

- variety of negative ions (incl. molecules)
- energy up to full target voltage equivalent
- negative ion fragmentation, some ions missing
- low sputter energy of molecules
- additional high-energetic positive ions (charge exchange)

Thank you
for your attention!

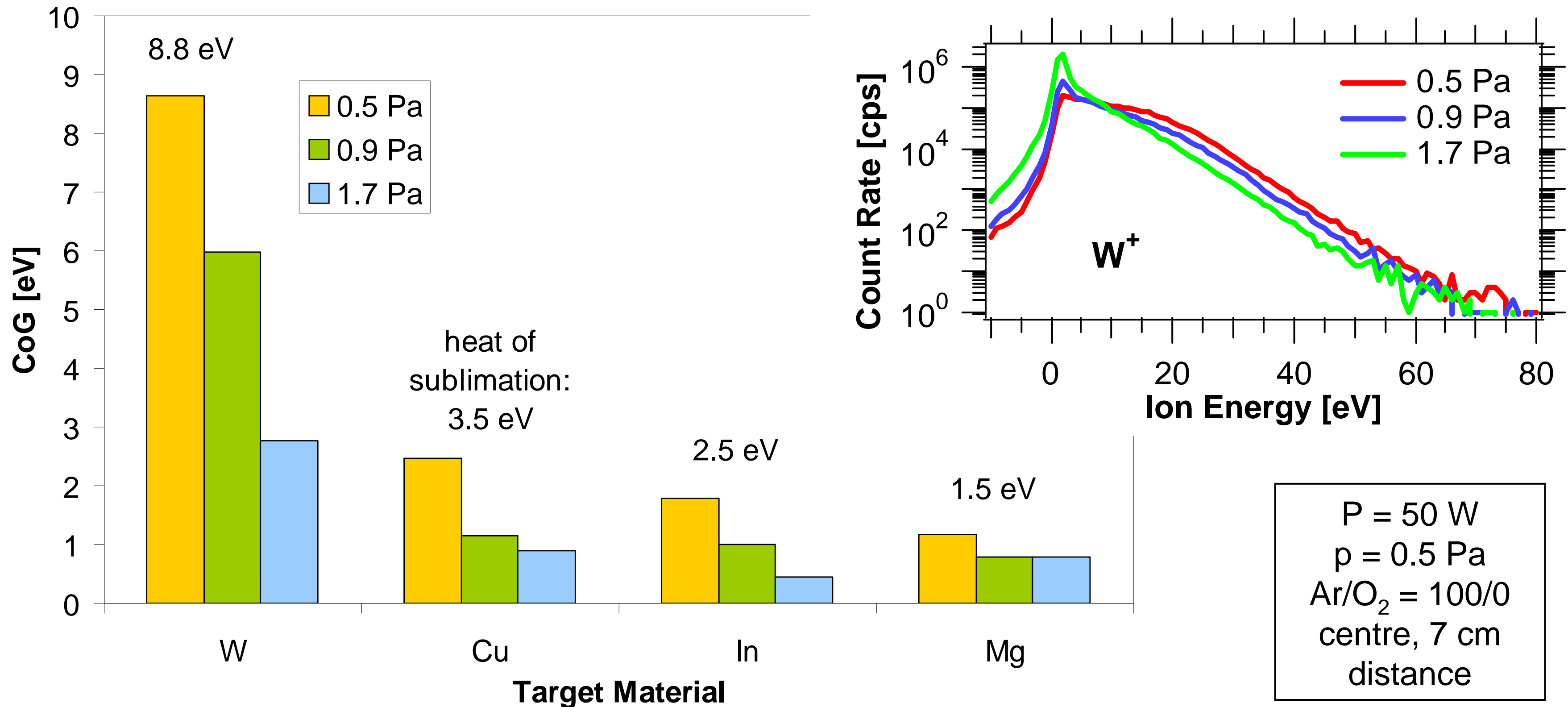
Magnetron Plasma – Typical Potential Distribution (d.c.)



- **positive ions from**
  - working gas (electron impact)
  - reflexted atoms (electron impact)
  - sputtered atoms (electron impact)
- **negative Ionen aus**
  - working gas (electron attachment)
  - emission from the target
  - sputtered atoms (electron impact)
- **various charge-exchange processes**

- **substrate:**
  - grounded (fixed)
  - with negative bias potential (fixed)
  - insulated (floating)
- **Measurement with the PPM is performed against ground potential.**

Positive Ion Distributions: Centre of Gravity for Metal Ions

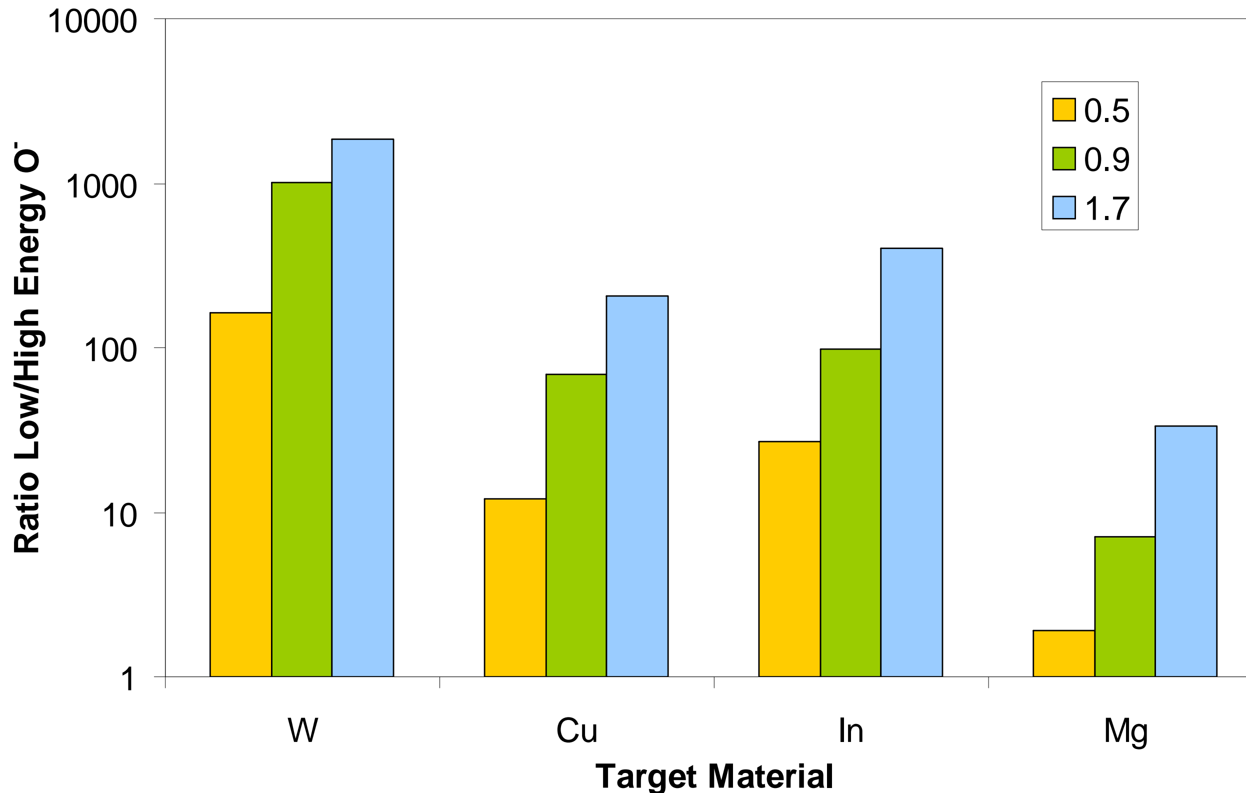


P = 50 W
p = 0.5 Pa
Ar/O_2 = 100/0
centre, 7 cm
distance

pressure increase: - high-energy tail (sputter distribution) ↓
- thermalised peak ↑

CoG: trend follows sublimation energy (better for heavy atoms – less efficient scattering)

Negative Ion Distributions: High- and Low-Energy Part



Parameter:
P = 50 W
p = 0.5 Pa
Ar/O_2 = 50/50
centre, 7 cm distance

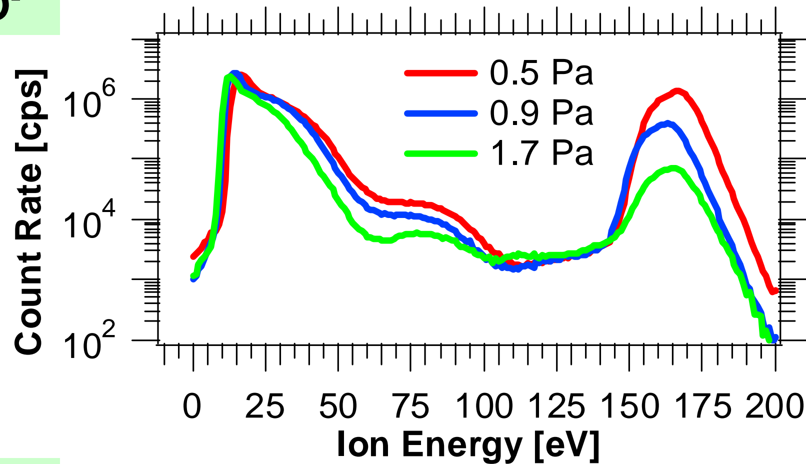
high-energy O^- represents γ_{ox}:

$\Rightarrow$ high ratio for WO_x (low γ_{ox}), lowest for MgO_x (high γ_{ox})

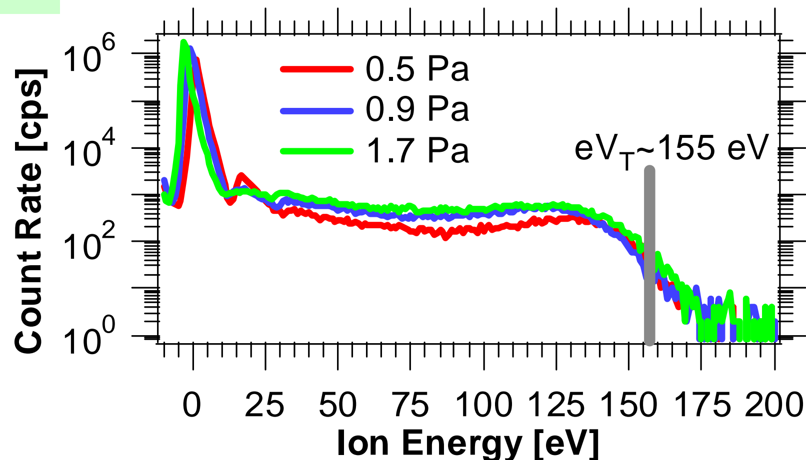
formation possibilities of low-energetic O^-:
(1) at the target sheath edge
(2) from high-energetic O^- by several collisions and electron re-attachment

Positive Ion Distributions (revisited): High-Energetic O^+

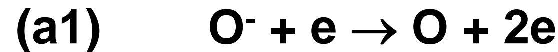
O^-



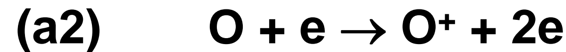
O^+



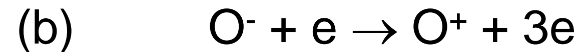
- O^- spans whole range up to eV_T
- charge exchange between target and substrate via electron impact:



(a1) $\mathbf{O^- + e \rightarrow O + 2e}$



(a2) $\mathbf{O + e \rightarrow O^+ + 2e}$



(b) $O^- + e \rightarrow O^+ + 3e$

⇒ **High-energetic O^+ results from O^- accelerated in the target sheath.**

⇒ Low-energy peak is still due to ions formed by electron-impact from the cold working gas in the plasma bulk.

Mg target , P = 50 W, Ar/O_2, centre, 7 cm distance