Target effective electron emission coefficients during reactive sputtering of Oxides and Nitrides

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Lay Out

LAY OUT

- Problem we want to tackle
- Measuring procedure
- Results for nitrides
- Results for oxides
- Discussion
- Conclusion

Thornton : revised

$$V_{\text{discharge}} = \frac{W_0}{\varepsilon_0 \varepsilon_i \boxed{m f \gamma_i}} \longrightarrow \text{original : } \gamma_{\text{effective}}$$

W_0 : effective ionisation energy

ε_i : ion collection efficiency (for magnetron : almost 1)

ε_0 : fraction of maximum possible number of ions (almost 1)

m : multiplication factor : accounts for ionisation in the sheath

f : effective ionisation probability : influenced by electron recapture

γ_i : ion induced secondary electron emission coefficient

* G. Buyle, “Simplified model for the DC planar magnetron discharge (PhD, UGENT,2005)

Emission mechanisms

Electron emission mechanisms under ion bombardment

Kinetic emission

- Coulomb interation
- Electron promotion

Typical for oxides

Potential emission

- Auger neutralisation
- Auger deexcitation

Typical for metals

$\gamma_{iK} > \gamma_{iP}$

Lay Out

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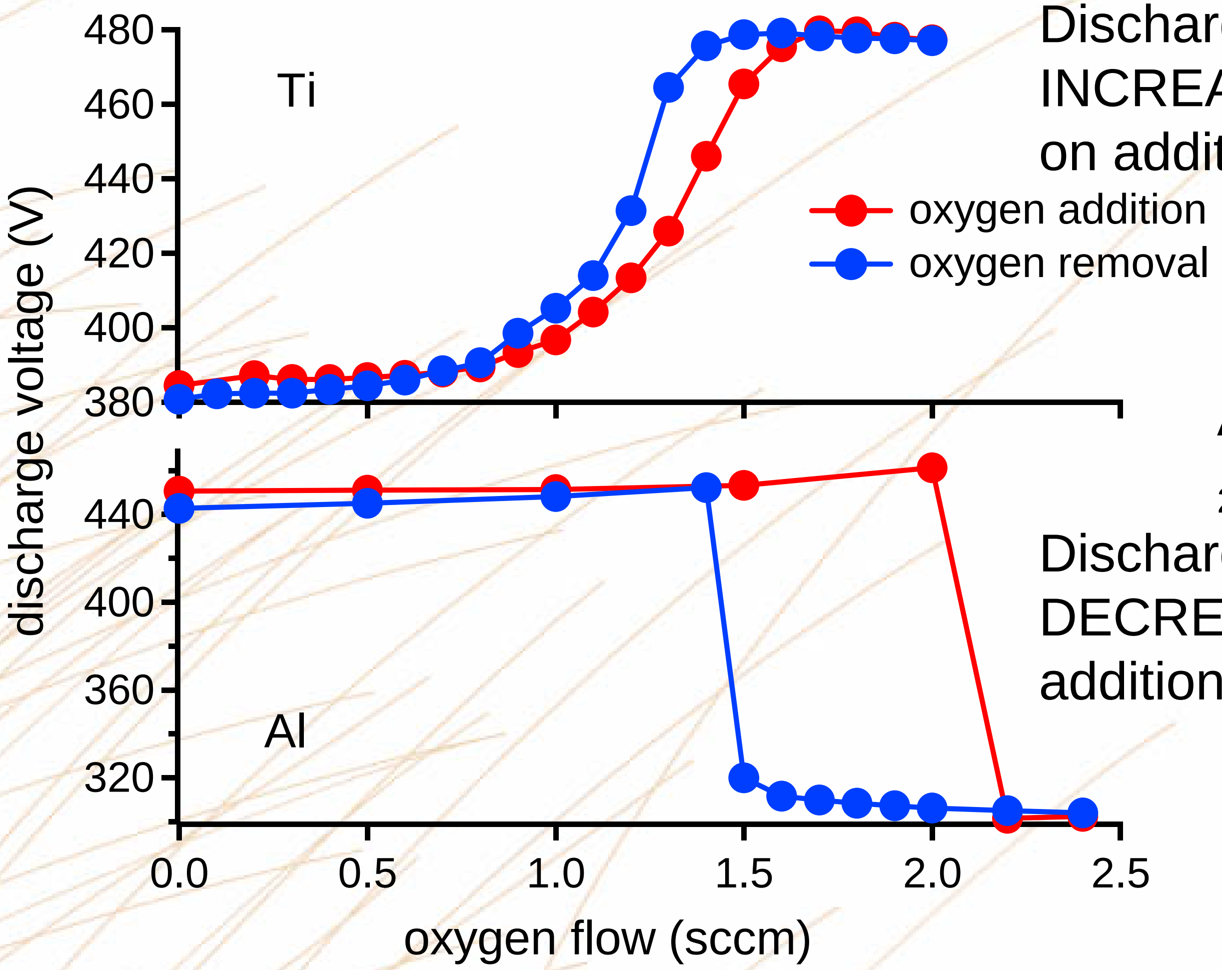
Hysteresis behaviour Ti/O_2 and Al/O_2



Ti/O_2

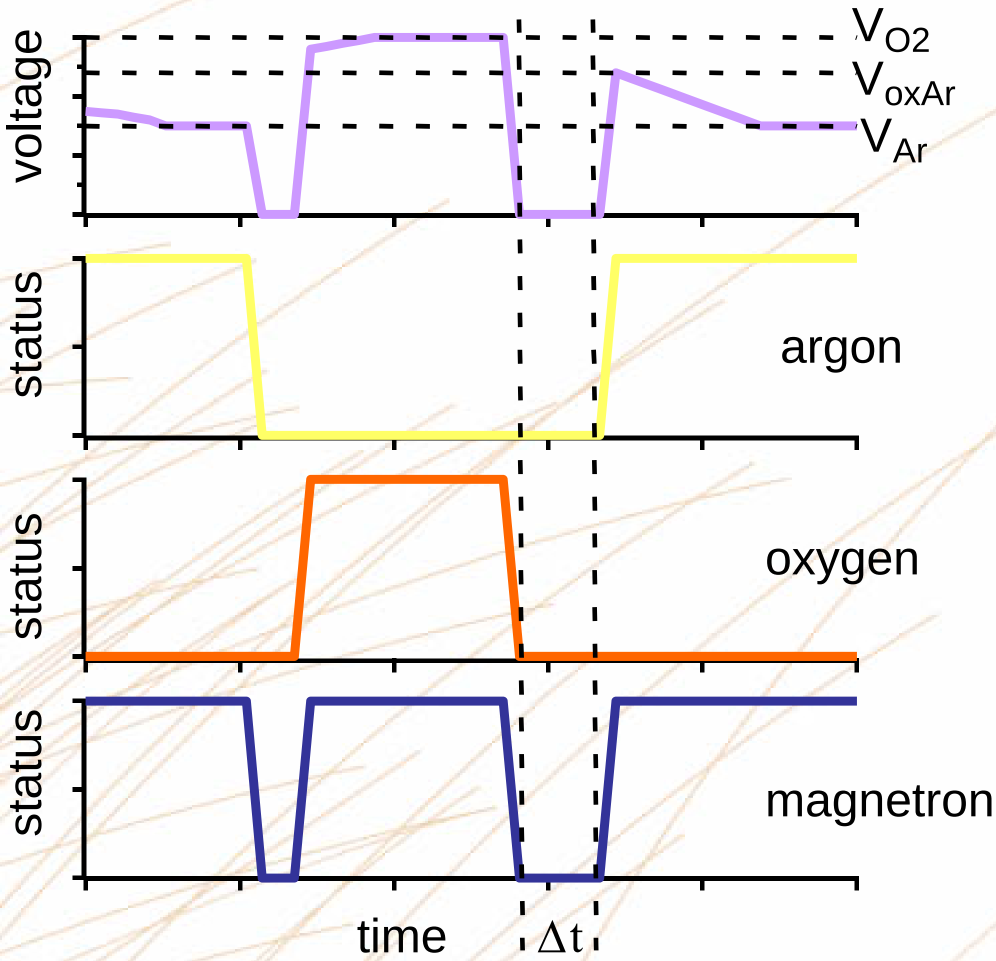
Discharge voltage INCREASES on addition of oxygen

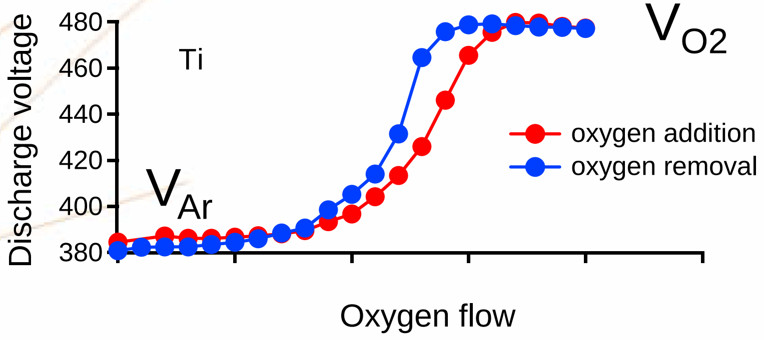
Al/O_2

Discharge voltage DECREASES on addition of oxygen

Measurements by S. Heirwegh

Measuring scheme





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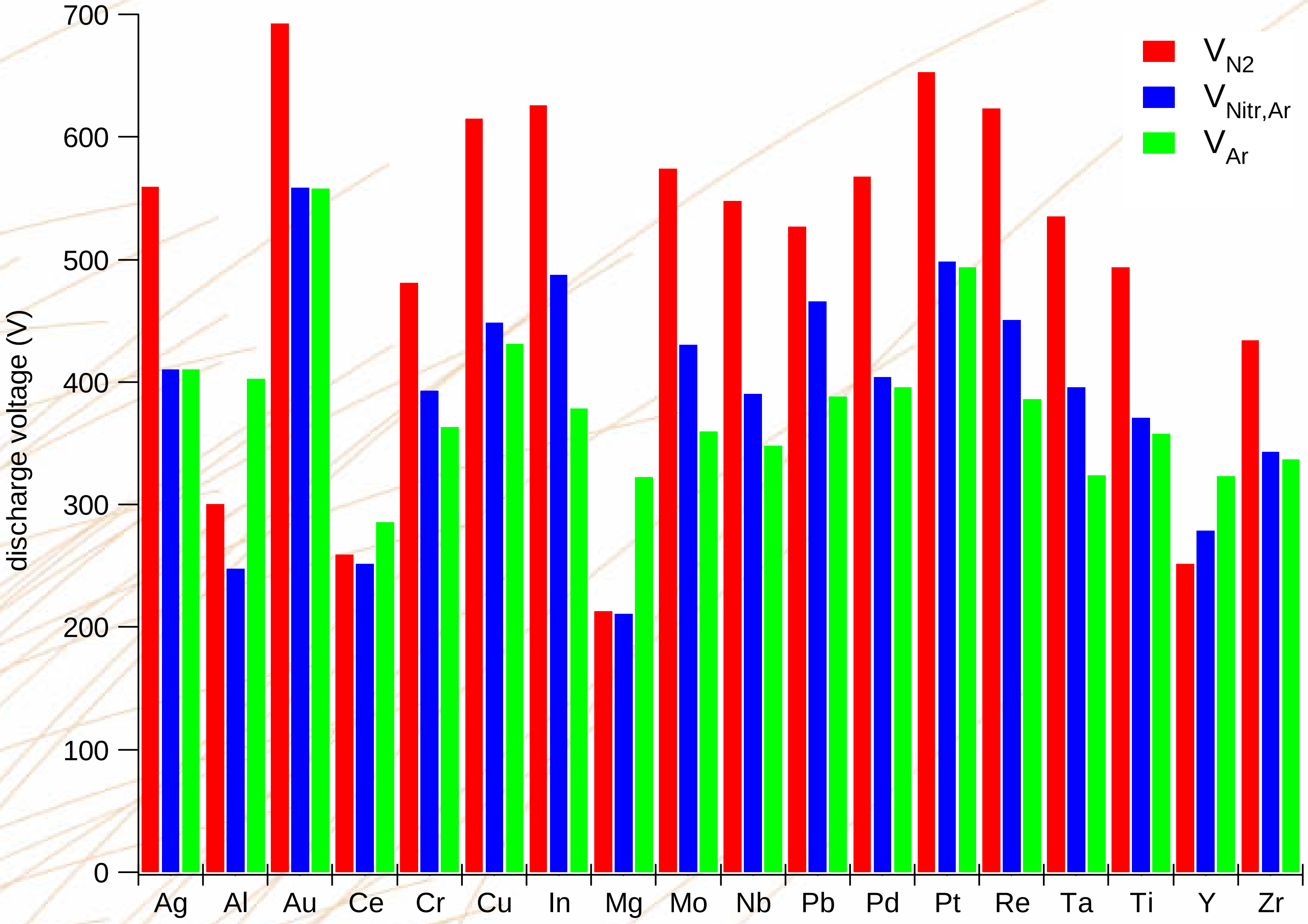
Discharge voltages: nitrides



Comparison between the discharge voltage measured in pure Ar (V_{Ar}), pure nitrogen (V_{N2}) and the discharge voltage of an nitrided target in pure Ar ($V_{nitr,Ar}$).

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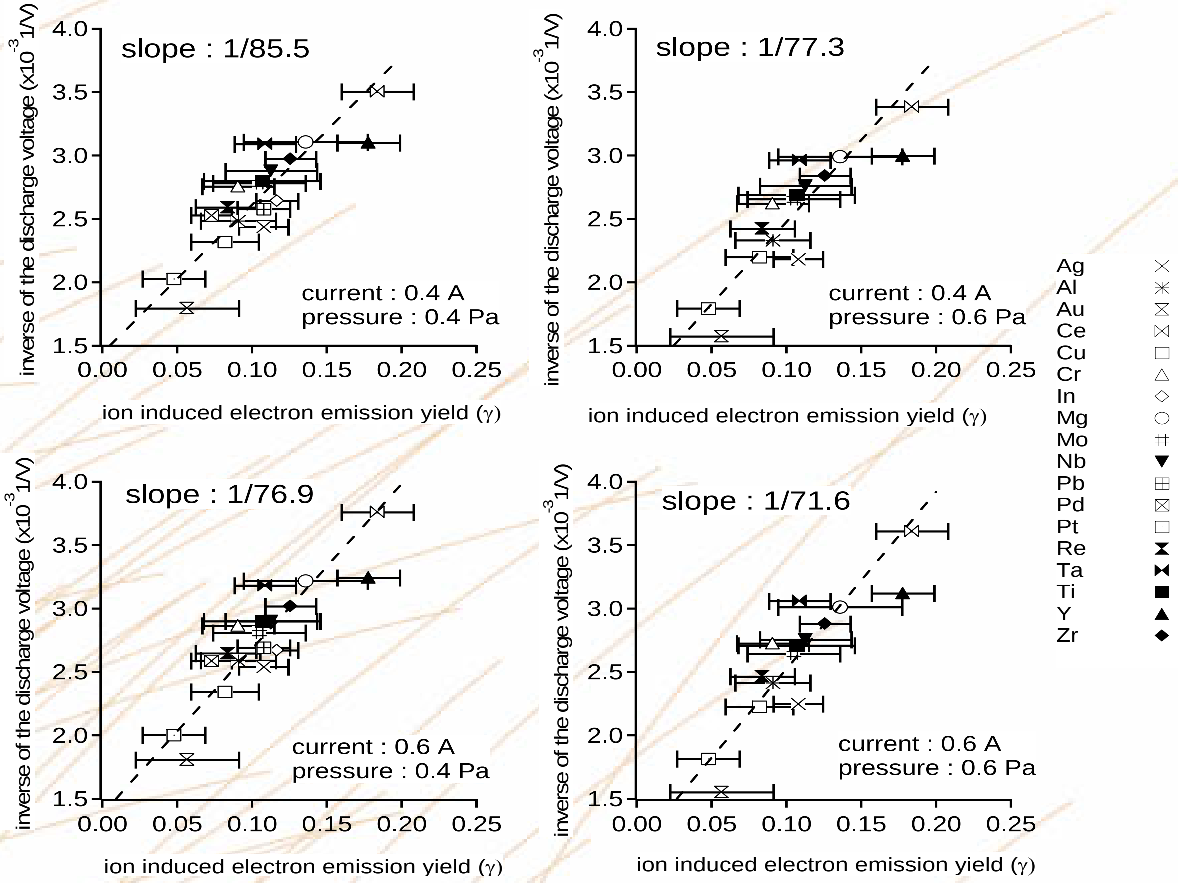
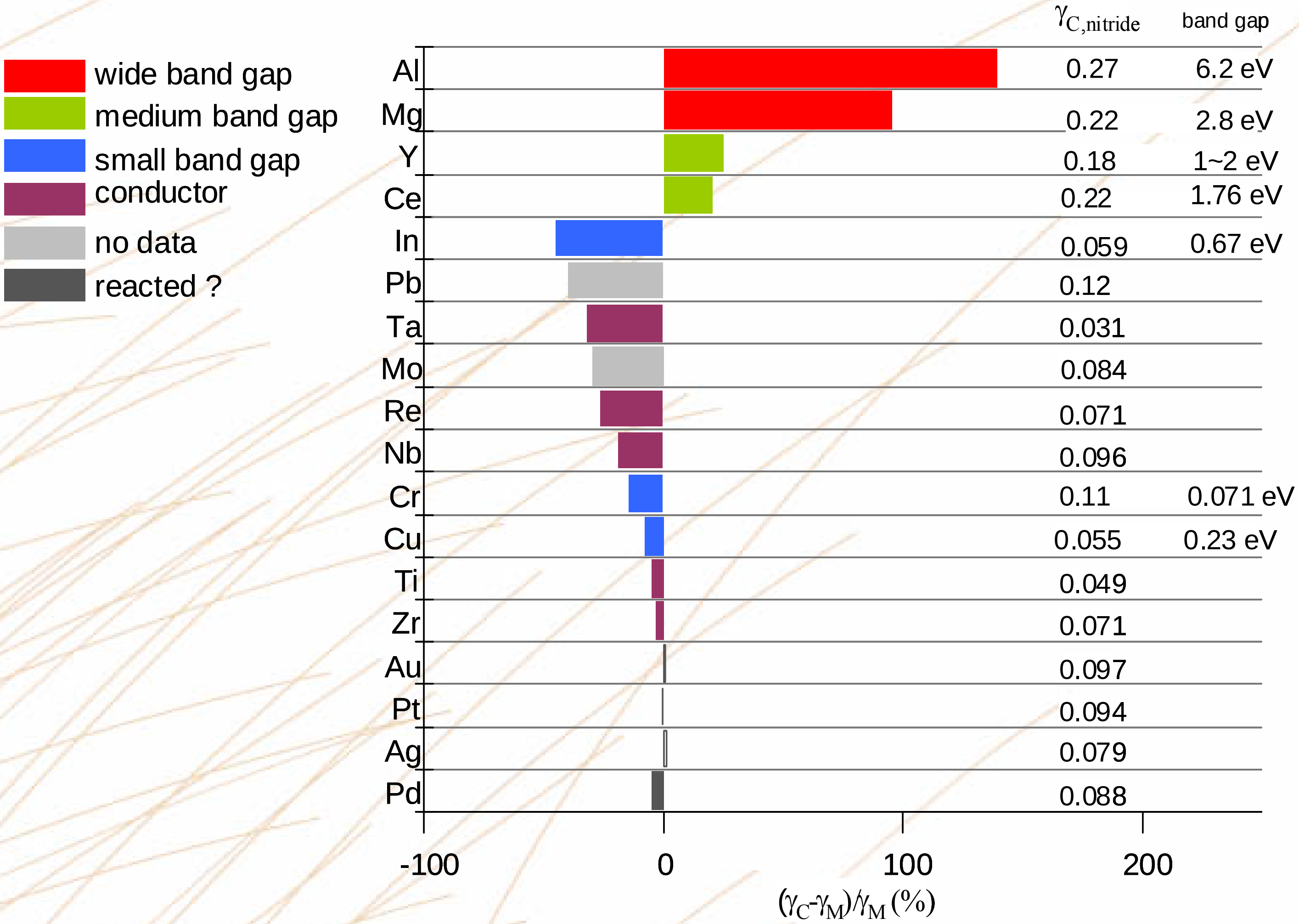
Inverse of discharge voltage versus γ_i



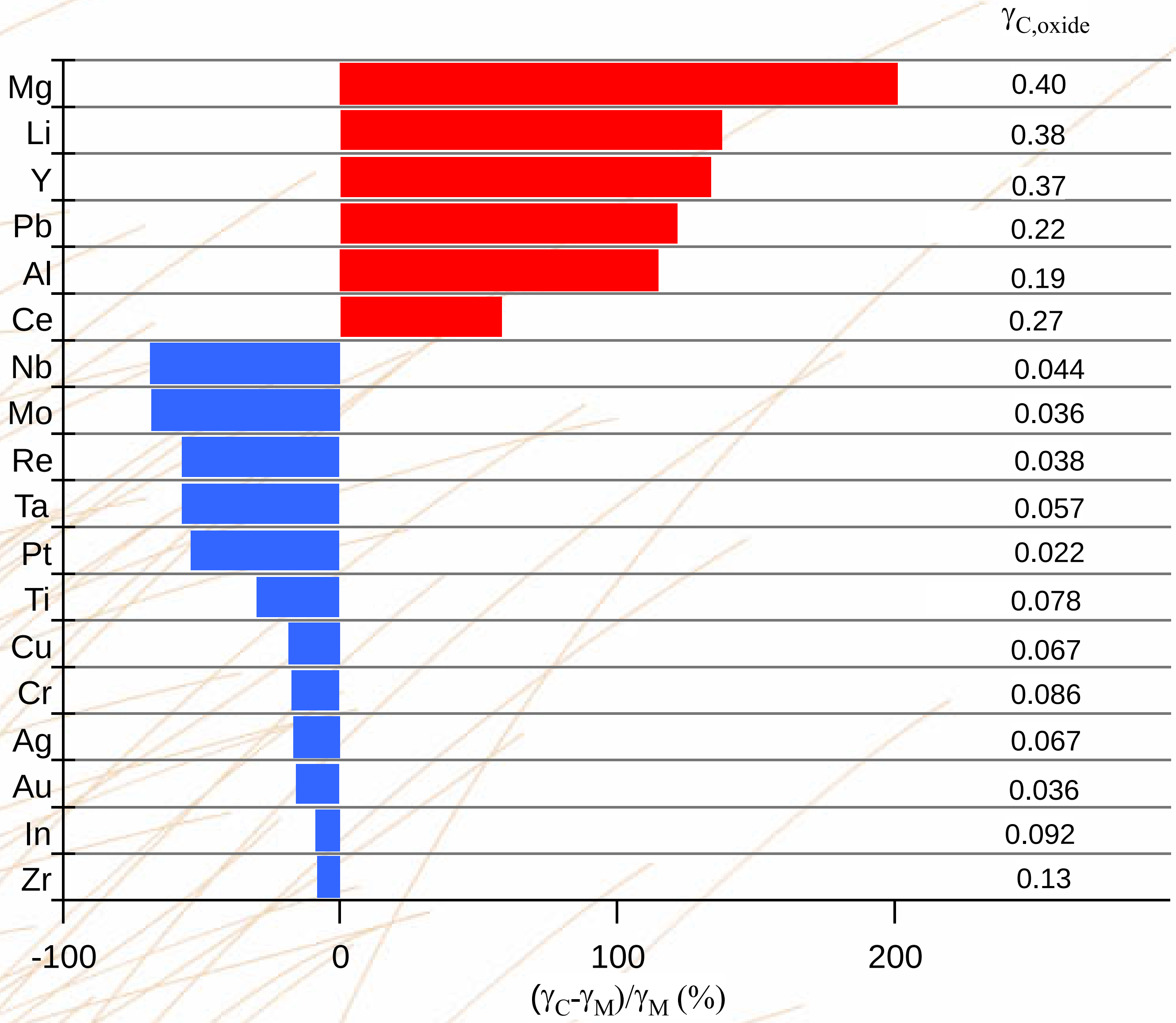
The inverse of the discharge voltage as a function of the ion induced γ_i for different target materials under several experimental conditions. The measurements were performed with a conventional two inch magnetron in a pure argon atmosphere. All targets had a purity of 99.99%. The dotted line is a linear fit. For all conditions the correlation coefficient has a value in the interval 0.87-0.89.

Relative variation of γ_i: nitrides



Relative change of the effective emission coefficient by nitridation of the metal target. γ_M and γ_C stands for respectively the γ_i of the metal and the compound.

Relative variation of γ_i: oxides



Relative change of the effective emission coefficient by oxidation of the metal target.

Problem

PROBLEM !

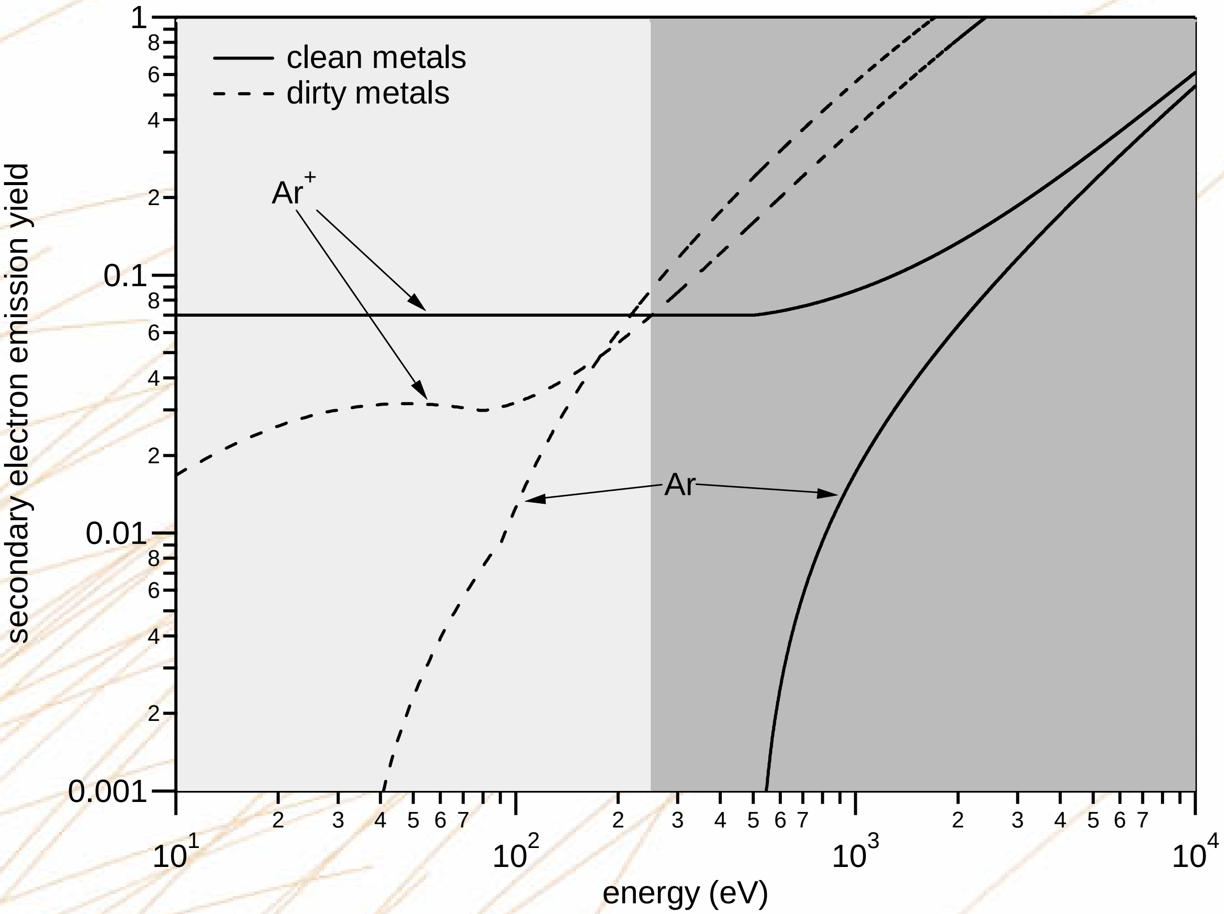
Oxides are wide gap materials

and

γ_i (oxide) >> γ_i (metal)

is expected

Phelps compilation



γ_i for argon ions and fast argon atoms bombardment (after [**Phelps1999**]) of clean metals and dirty metals. Above 250 eV ions the γ_i is substantially higher for a dirty, oxidized surfaces as compared to the clean metal surface.

Wittmaack's conclusions

Wittmaack 1999

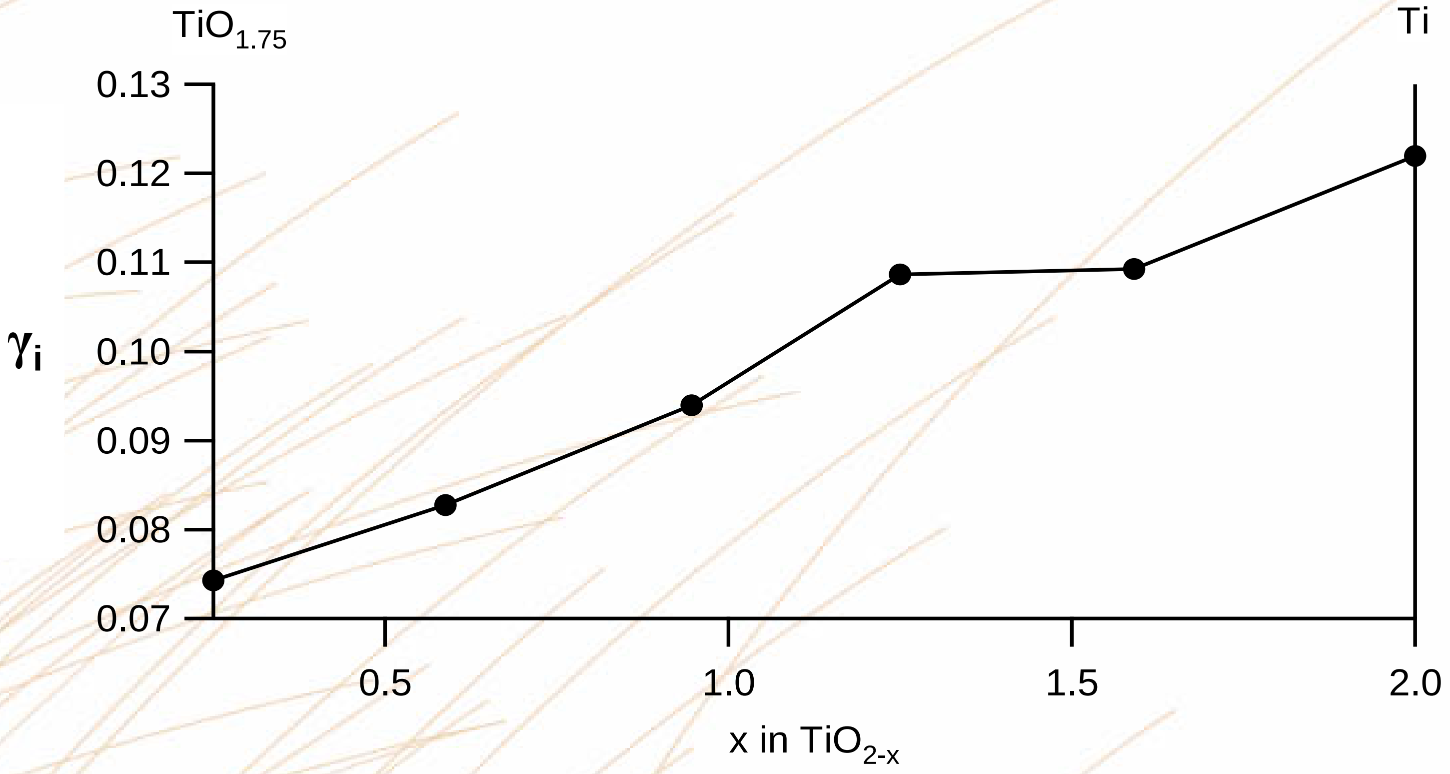
1. Implantation of low energy oxygen ions in Si
   - 1.1: γ_i proportional to the surface coverage of SiO_2
2. Sputter etching of SiO_2 with Ne^+
   - 2.1: rapid decrease of γ_i
   - 2.2: preferential loss of oxygen
   - 2.3: γ_i of suboxide SiO_x $(x < 2)$ shows a negligible variation as compared with that of the parent metal

Suboxides

Powder composition for the production of the titania targets

TiO_2 (wt. %)	Ti (wt. %)	Target phase composition	x in TiO_{2-x}
100	0	TiO_2 (rutile)	0.25
80	20	Ti_2O_3 (50%), TiO (50%)	0.6
65	35	TiO	1
50	50	TiO (small amount Ti_2O)	1.25
30	70	Ti_2O	1.6

γ_i of Ti-suboxides



Calculated effective γ_i as a function of the target stoichiometry for titania suboxide targets.

Effect of electronic properties

What can we conclude ?

Electronic properties of (Ti) suboxide surfaces are completely different as compared to the surface properties of the basic oxides.

Remember DC-sputtering of TiO_x targets!

Model

- Reactive magnetron sputtering with oxygen:

  ⇒ Formation of oxide layer on target by shallow oxygen implantation

  ⇒ Due to preferential sputtering, the target oxides **can** be reduced to suboxides with low γ_i values

  ⇒ Discharge voltage will increase under poisoning condition

- Which target materials are sensitive to reduction and the formation of suboxides ??
- Are there target materials which do not form suboxides under ion bombardment ??

Surprise

From literature:

1. The oxides of Al, Mg, Ce, Y sputter congruently
   → no preferential sputtering
   → no formation of suboxides
   → surface composition = bulk composition
   = fully oxidized material

   These oxides are exactly the high γ_i oxides !
2. Nitrides show little or no preferential sputtering
   → surface composition = bulk composition
   → wide gap nitrides remain wide gap materials under ion bombardment and vice versa

- Electronic properties of both classes of target materials are not affected by ion bombardment !!
- Can we predict this behaviour ?

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Reduction factor

Surface reduction factor R can be estimated:

1. $$R = \frac{(X_M/X_O)^s}{(X_M/X_O)^b}$$

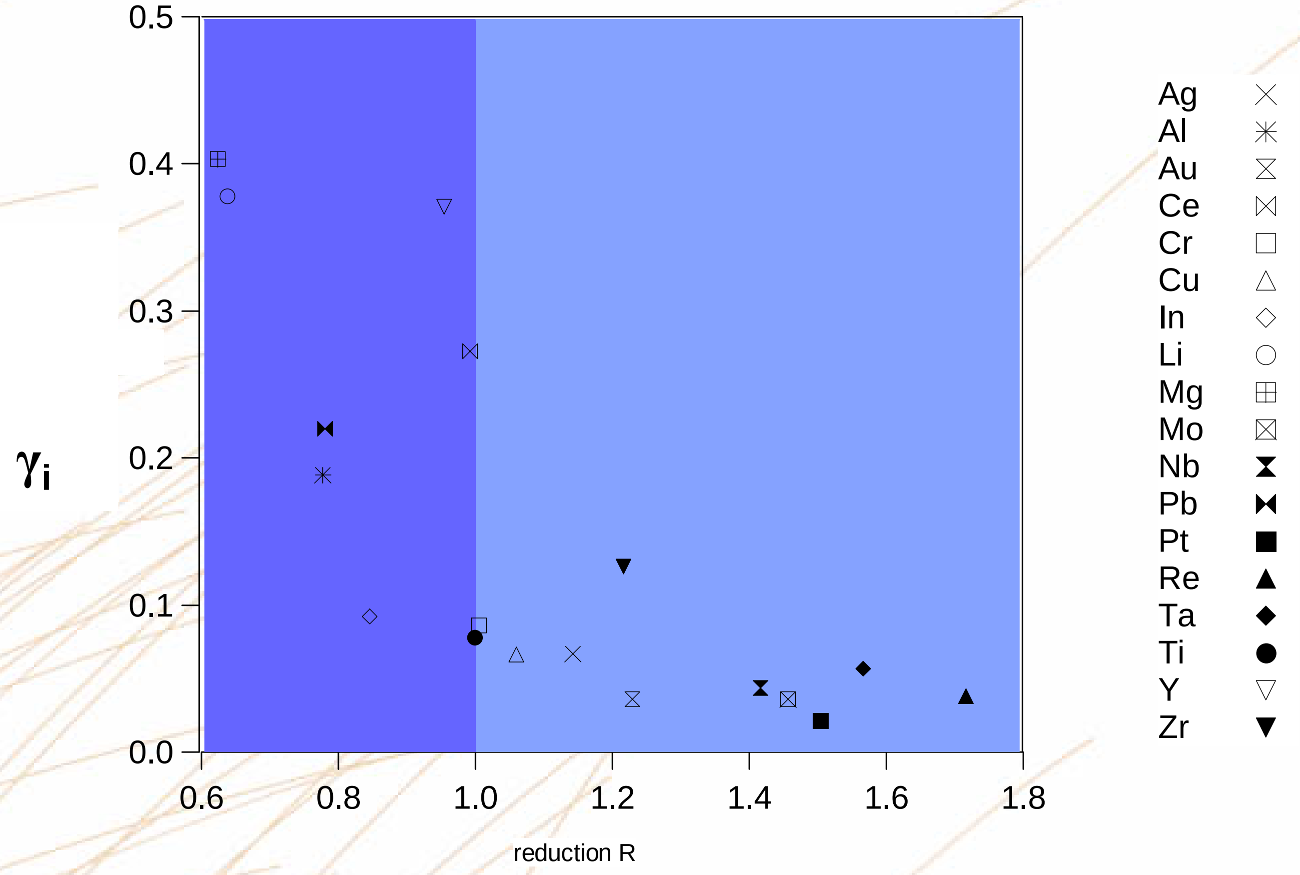
2. $$\left(\frac{X_M}{X_O}\right)^s = \frac{Y_O}{Y_M}\left(\frac{X_M}{X_O}\right)^b$$ preferential sputtering (Malherbe)

3. $$\frac{Y_O}{Y_M} = \left(\frac{AM_M}{AM_O}\right)^{2m}\left(\frac{U_M}{U_O}\right)^{1-2m}$$ collision cascade (Sigmund)

AM_M, AM_O : atomic masses

U_M, U_O : binding energies

γ_i versus R



The calculated γ_i for oxides as a function of the reduction factor R calculated with the model of Malherbe et al. (with m=0.05). Nitrides show no preferential sputtering

Conclusion

1. Electronic properties of the target surface under ion bombardment (preferential sputtering or not) are the dominant factors in the understanding of the ion induced secondary electron emission.
2. Small gap materials and metals have a low γ_i
   - oxides of Nb, M_o, R_e, Ta, Ti, Cu, Cr, In, Zr which under ion bombardment reduce to suboxides
   - nitrides of In, Pb, Ta, M_o, R_e, Nb, Cr, Cu, Ti, Zr, Pd which are either semiconductors or conducting nitrides. These materials show no or very small preferential sputtering

Potential emission is the dominant mechanism for production of secondary electrons (low γ_i)

→ Discharge voltage increases upon poisoning !

Conclusion

3. Wide gap materials or insulators have a high γ_i
   - oxides of Mg, Li, Y, Pb, Al, Ce which are not subjected to preferential sputtering under ion impact
   - nitrides of Al, Mg, Y, Ce which are also not sensitive to preferential sputtering (as all nitrides under study)

Kinetic emission is the dominant mechanism of secondary electron emission (high γ_i)

→ Discharge voltage decreases upon poisoning !

4. The hysteresis behaviour under reactive sputtering is understood and predictable !

Acknowledgements

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