Tantalum oxynitride films with smoothly tunable composition, electronic structure and properties

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DEPARTMENT OF PHYSICS

NTIS

Acknowledgment

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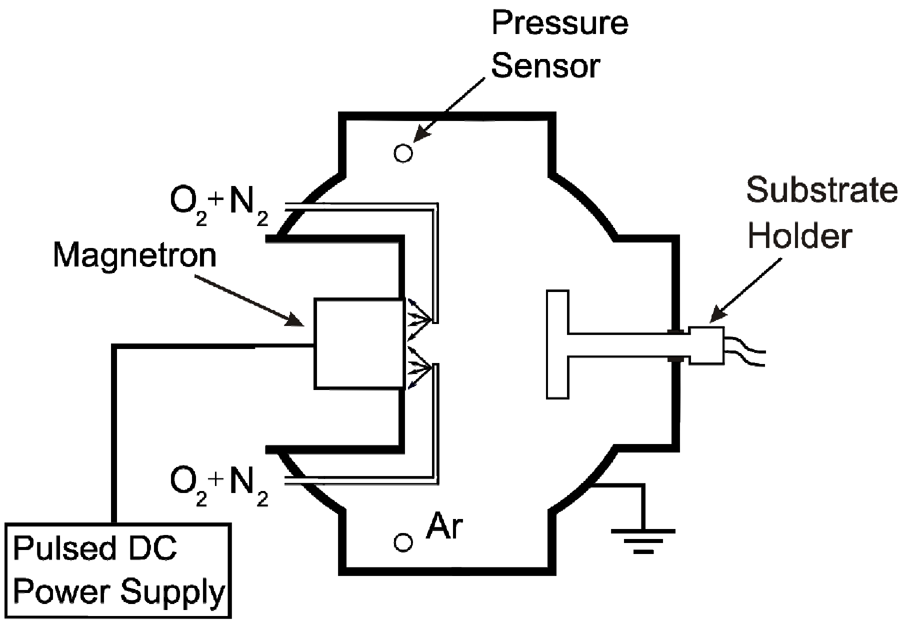
Outline

- How to prepare all films, including the O-rich ones, at high deposition rates (avoiding target poisoning)
- How to prepare oxynitride films with elemental compositions smoothly tuned in the full range from oxides to nitrides (despite significantly higher reactivity of O_2 than that of N_2)
- What are the relationships between the elemental composition and the structure and properties of the films

[J. Rezek, J. Vlcek, J. Houska, R. Cerstvy, Thin Solid Films 566, 70 (2014)]

Deposition technique (HIPIMS with RGFC)

- High-power impulse reactive mag. sputtering in $Ar+O_2+N_2$ using patented **reactive gas flow control (RGFC)**
- RGFC: programmable logical controller opens / closes O_2+N_2 flux using pre-selected critical values of:
  - dischage current (responds more sensitively e.g. for Zr)
  - or O_2+N_2 partial pressure (responds more sensitively e.g. for Ta)



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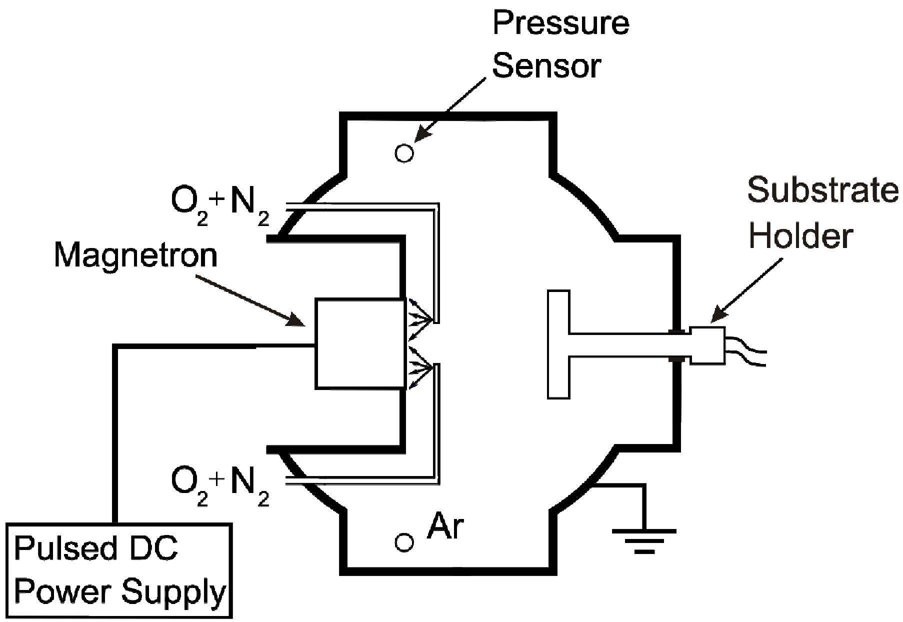

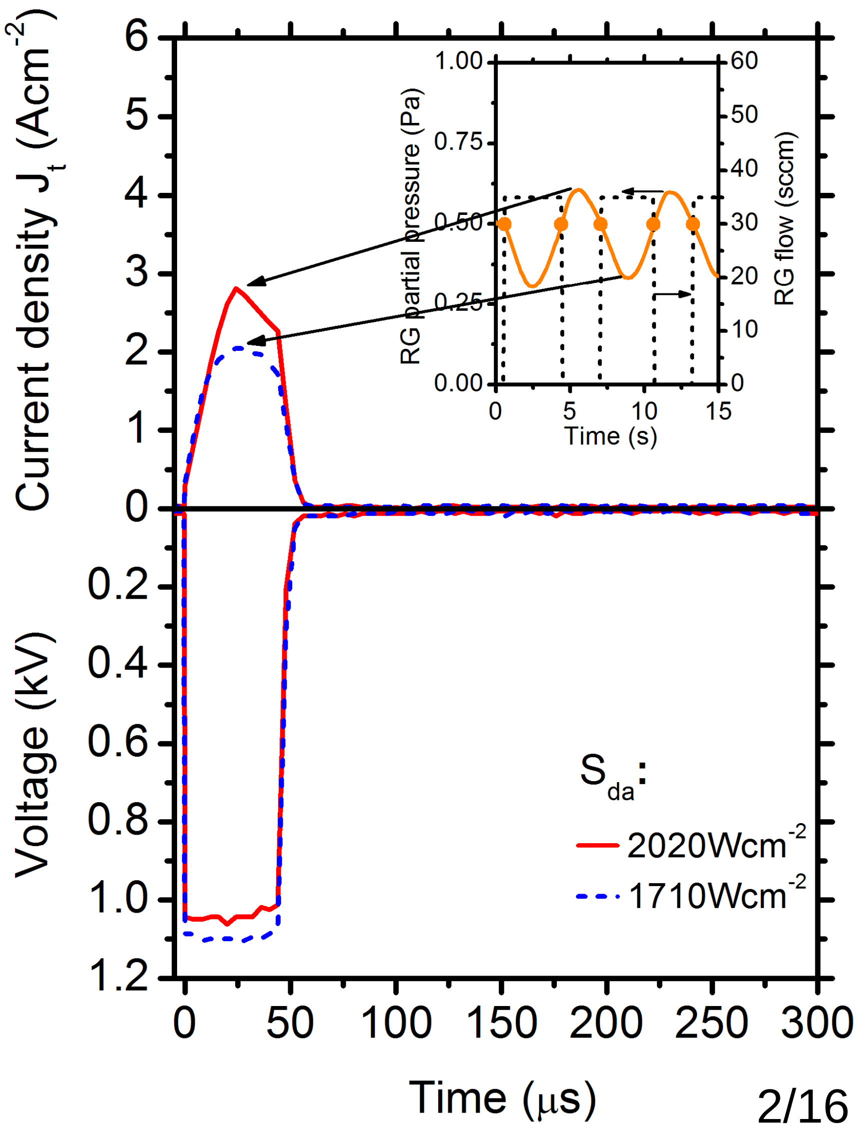

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$\Downarrow$

- No microarcs and discharge instabilities resulting from compound mode
- No understoichiometry resulting from metallic mode

[J. Vlcek et al., European patent application No. 13155936.1-1353]

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- Densified (n_{550} = 2.19-2.22) stoichiometric ($k_{550} \leq 6\times10^{-3}$) **$ZrO_2$ at deposition rate 140 nm/min**
- Densified (n_{550} = 2.09-2.15) stoichiometric ($k_{550} \leq 1\times10^{-4}$) **$Ta_2O_5$ at deposition rate 345 nm/min**

[J. Vlcek, J. Rezek, J. Houska, R. Cerstvy, R. Bugyi, Surf. Coat. Technol. 236, 550 (2013)]
[J. Vlcek, J. Rezek, J. Houska, T. Kozak, J. Kohout, Vacuum 114, 131 (2015)]

Smooth control of O/N

Challenges

- Extra O coming from the poisoned sputter target
- O_2 has higher reactivity than N_2
  (easier dissociation on and subsequent bonding to film surf.)

Solution

- Reactive gas flow control ⇒ no/limited target poisoning
  ⇒ oxygen and nitrogen on the same "starting line"
- Proper location and orientation of the reactive gas inlets
  (in front of the target and towards the target, respectively)
  ⇒ high dissociation of both O_2 and N_2
  ⇒ ~~high reactivity of O_2, low reactivity of N_2~~
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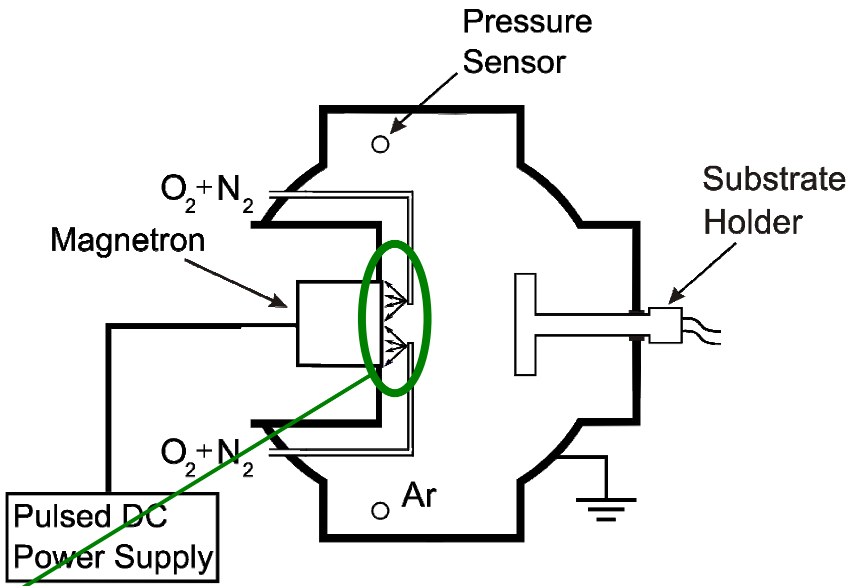

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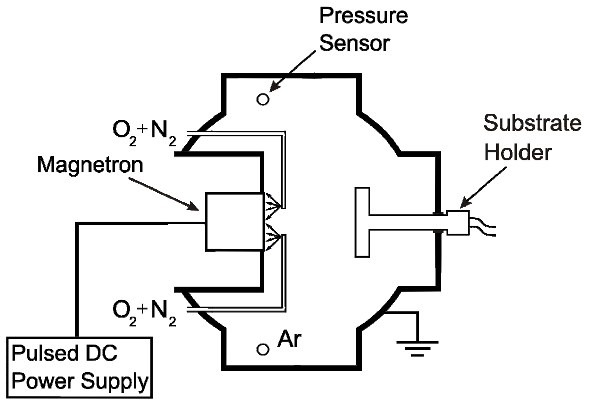
high reactivity of O, high reactivity of N

TaON - deposition conditions

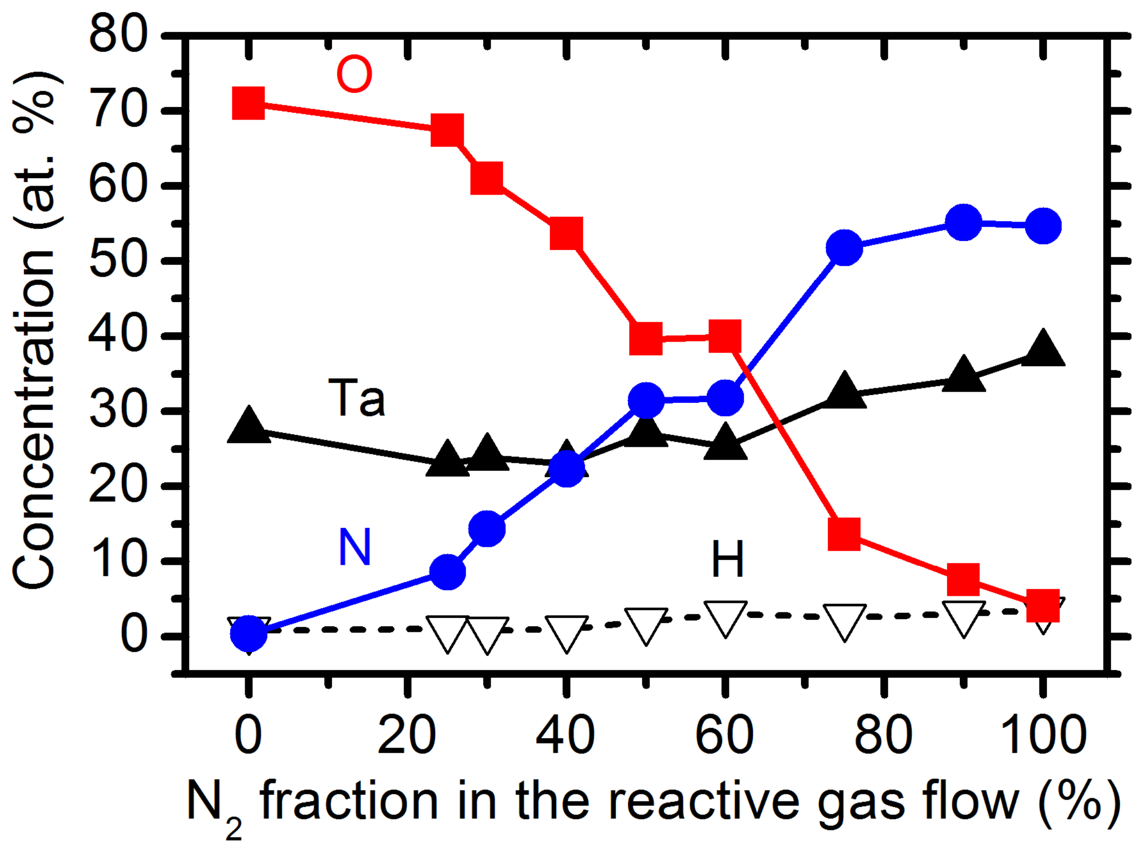
- HIPIMS of Ta target (100 mm in diam., direct water cooling)
- $Ar+O_2+N_2$ gas mixture (pressure close to 2 Pa)
- TruPlasma 4002 (TRUMPF Huettinger) with RGFC
  - repetition frequency 500 Hz
  - voltage pulse length 50 µs
  - duty cycle 2.5 %
- Average target power density
  - 50 Wcm^{-2} during deposition
  - up to 2390 Wcm^{-2} in a pulse



- Si and glass substrate (floating potential, T < 250 °C)

TaON - smoothly varied elemental composition

- Indeed, the higher reactivity of oxygen has been almost suppressed (e.g. 50% O_2 + 50% N_2 $\Rightarrow$ $Ta_{27}O_{40}N_{31}$)
$\Rightarrow$ ability to prepare any oxynitride composition



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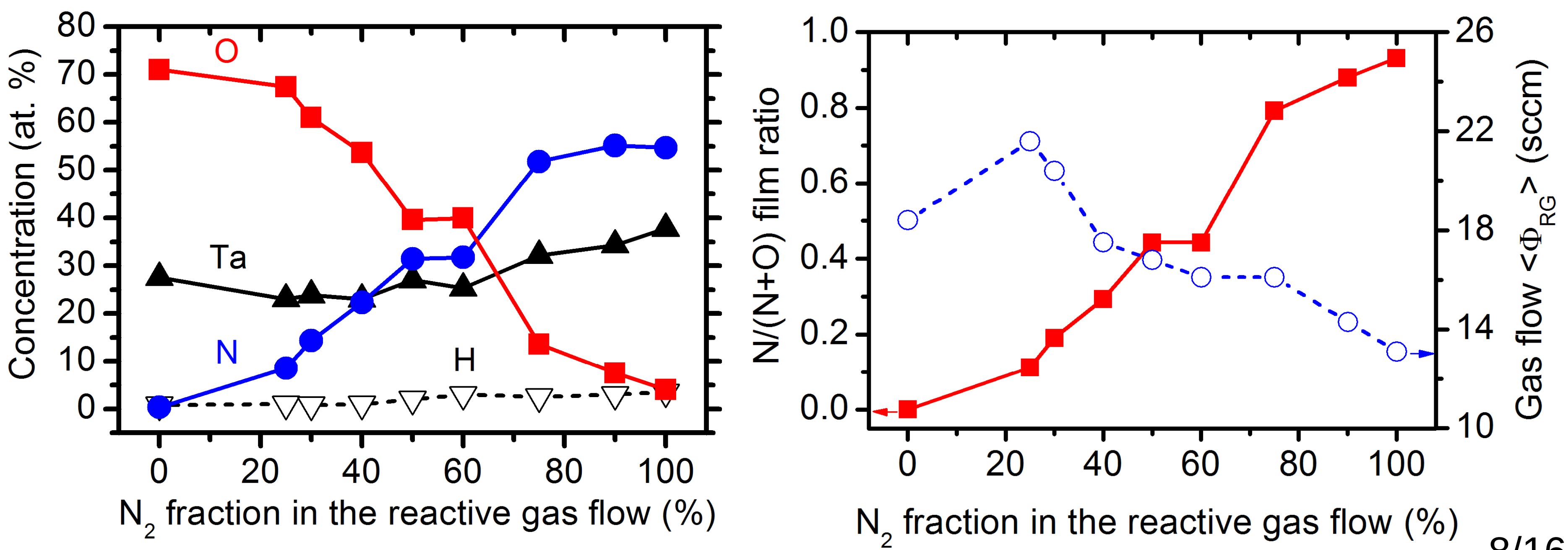
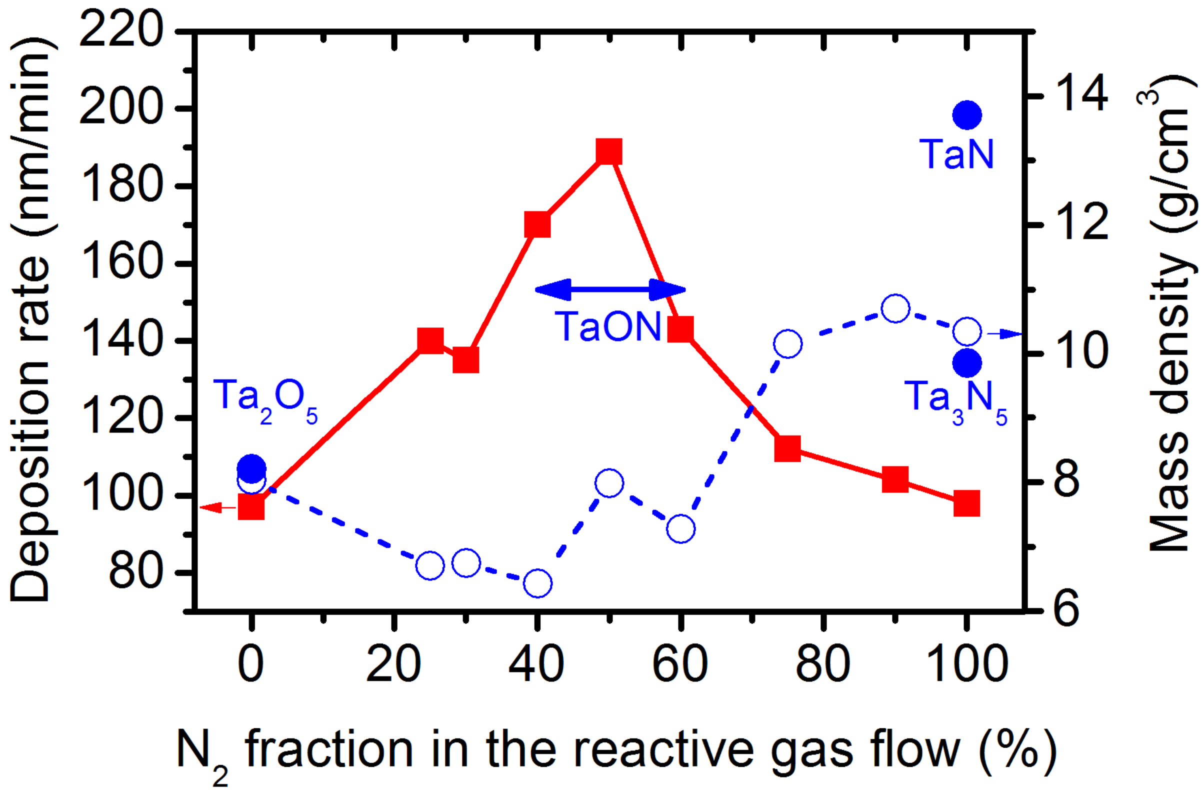
- Lower O+N content (higher Ta content) $\Rightarrow$ lower O_2+N_2 flow (i.e. RGFC $\Rightarrow$ as much reactive gas as we need, no more)



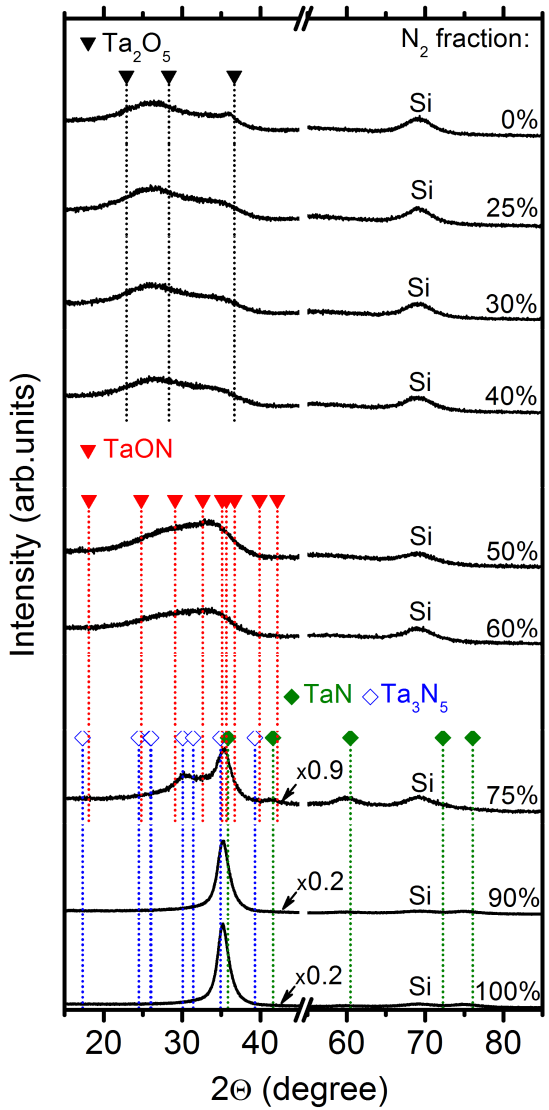
TaON - deposition rate

Focus on O_2 & N_2 dissociation ⇒ short duty cycle 2.5% ⇒
97 nm/min for dense oxide, up to 190 nm/min for oxynitride

(Focus on dep. rate ⇒ duty cycle 10% ⇒ 345 nm/min for oxide)



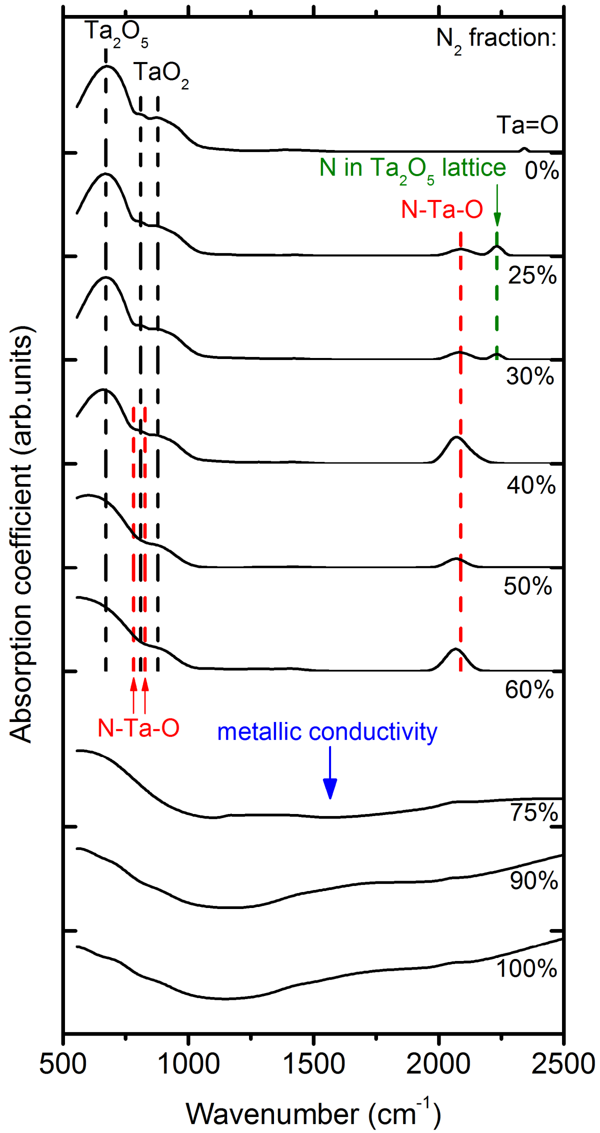
TaON - structure (XRD)



- XRD:

$Ta_2O_5 \rightarrow$ TaON $\rightarrow Ta_3N_5$ / TaN

TaON - structure (FTIR)



- XRD:

  $Ta_2O_5 \rightarrow$ TaON $\rightarrow Ta_3N_5$ / TaN

- FTIR:

  $Ta_2O_5 \rightarrow Ta_2O_5$-based solid solution

  $\rightarrow TaO_xN_y \rightarrow$ TaN (metallic conductivity)

TaON - optical constants

- Transparent (O-rich) compositions: **Cody-Lorentz dispersion**

$\varepsilon_2 = ABE_nE/[(E^2 - E_n^2)^2 + B^2E^2]\ (E-E_g)^2/[(E-E_g)^2 + E_p^2]\quad E \geq E_g+E_t$

Lorentz term, L(E) *Cody term, G(E)*

$\varepsilon_2 = L(E_g+E_t)\ G(E_g+E_t)\ (E_g+E_t)/E\ \exp[(E-E_g-E_t)/E_u]\quad E < E_g+E_t$

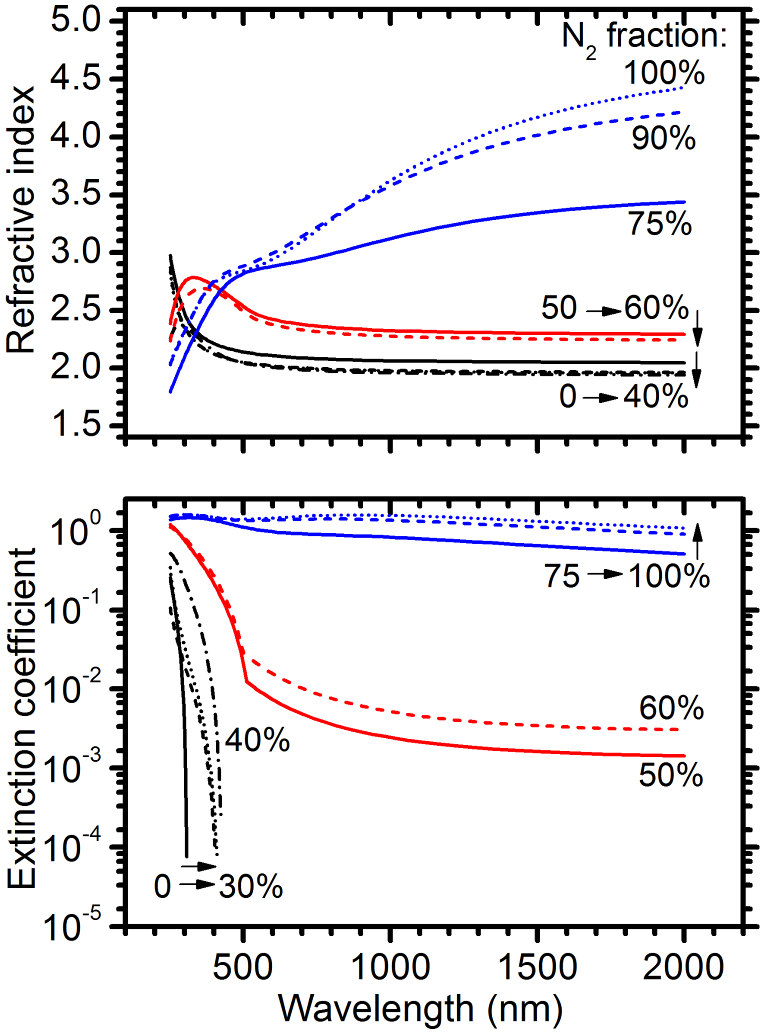
(Urbach tail)

fitted parameters discussed below include

- $\mathbf{E_g}$ ("narrowly defined" optical gap)
- $\mathbf{E_g+E_t}$ ("widely defined" optical gap - incl. "defect" states)
- **B** (oscillator broadening)

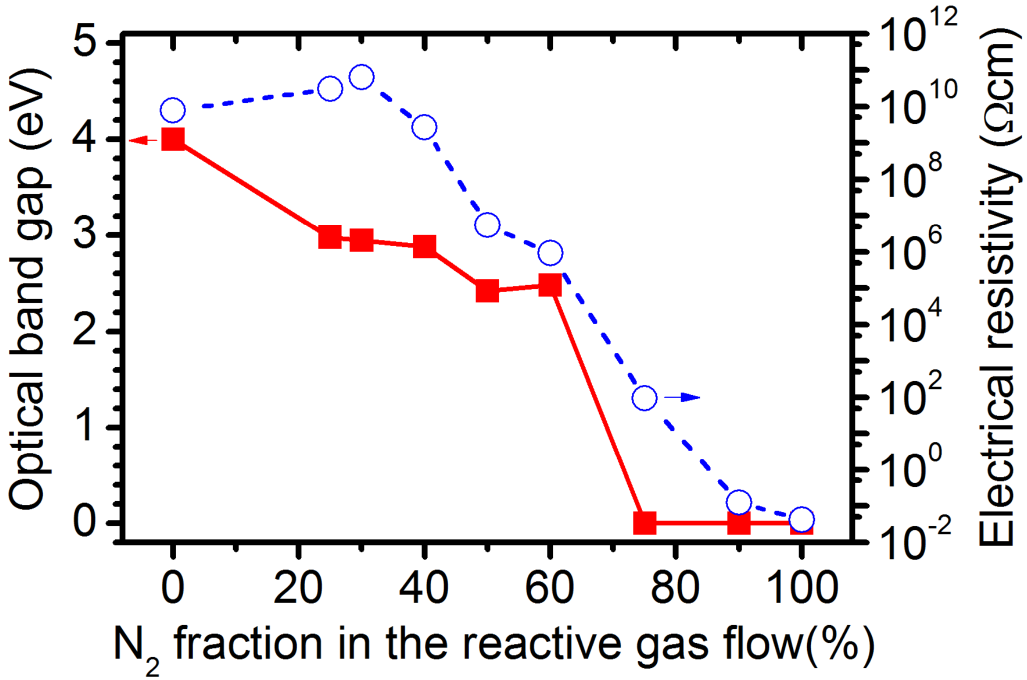
- Opaque (N-rich) compositions: Lorentz oscillators

TaON - optical constants



- **0% N_2 in reactive gas (RG):** E_g = 4 eV, E_t = 0, n_{550} = 2.12 ⇒ pure & densified Ta_2O_5
- **25-40% N_2 in RG:** narrower gap (E_g = 3 eV), sharp band edge (E_t = 0), similar n_{550} of 2.02-2.03 ⇒ Ta_2O_5-based
- **50-60% N_2 in RG:** narrower gap (E_g+E_t = 2.5 eV), defects (E_t = 0.2-0.25 eV) ⇒ strong Urbach tail (k_{550} = 0.006-0.010)
- **75-100% N_2 in RG:** metallic (TaN-based)

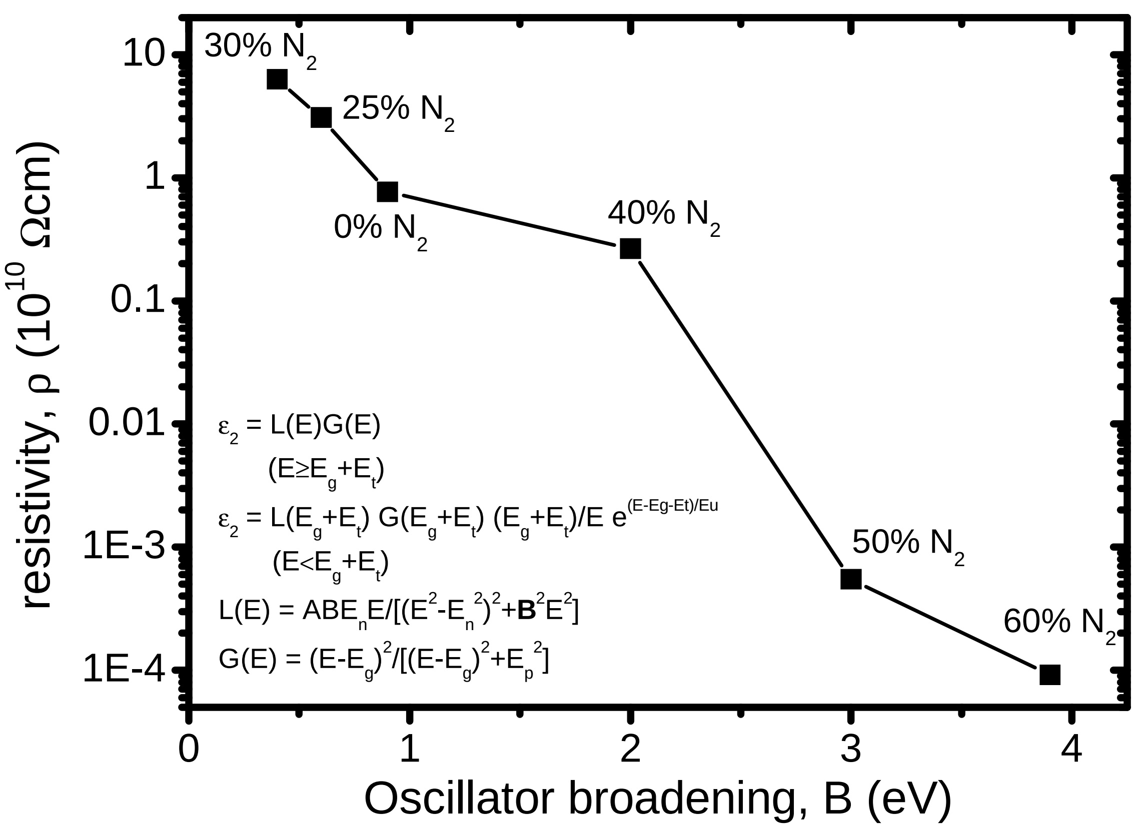
TaON - optical gap (E_g+E_t), electrical resistivity



- **0% N_2 in RG:**
  4 eV
  7.7×10^9 Ωcm
- **25-40% N_2 in RG:**
  3 eV
  up to 6.3×10^{10} Ωcm
- **50-60% N_2 in RG:**
  2.5 eV, defects (high E_t)
  $\Rightarrow$ down to 9.1×10^5 Ωcm
- **75-100% N_2 in RG:**
  opaque, down to
  4.2×10^{-2} Ωcm

TaON - explanation of electrical resistivity (ρ)

- Problem: non-monotonous dependence of ρ on O/N
- Solution: **monotonous dependence of ρ on oscillator broadening** (high B ⇒ defects ⇒ more free charge carries)



Conclusions

- Pulsed reactive gas flow control ⇒ stoichiomentric oxides and oxynitrides at hundred(s) nm/min
- O is only slightly more reactive than N ⇒ dissociation (gas inlet position!) leads to tunable oxynitride compositions
- TaON: smoothly varied composition, structure, electronic structure (band gap), optical properties, electrical resistivity
- Ability to achieve visible range optical gap (e.g. 50% O_2 + 50% N_2 ⇒ $Ta_{27}O_{40}N_{31}$ with 2.5 eV) ⇒ research in the field of visible-light photocatalysis