Growth and electronic properties of TiO_2–based thin films

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Outline

- History of development
- Motivation
- Overview of activities
- Basics of transparent conductive oxides
- Challenges and objectives
- Experimental approach
- Basics of magnetron sputtering
- Direct growth of TiO_2-based TCOs
- Two-step formation process
- Summary and Outlook
- Acknowledgements

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History of development

- **CdO**: bulk 1902 (Streintz), thin film 1907 (Badeker)
  - CdO-based compounds:
    - best electrical properties
    - optical transmittance is not optimal, toxic material
- **SnO_2**: first patent 1938 (Littleton), films on glass 1942 (McMaster)
  - SnO_2:F is dominating on the market (Asahi Glass)
    - established technology, integration in large area glass production
    - fluorine-containing precursors, high environmental footprint
- **In_2O_3**: first patent 1947 (Zunick)
  - In_2O_3:Sn (ITO)
    - standard technology (sputtering), the best material available
    - expensive, metallic indium supply problems
- **ZnO:Al**: first publication 1971 (Wasa)
    - early stages of commercialization, cost-efficient production
    - environmentall stability problems
- **TiO_2:Nb**: first publication 2005 (Furubayashi)

Review: Ingram et al, *J. Electroceram.* 13, 167 (2004)

Furubayashi et al, *Appl. Phys. Lett.* 86, 252101 (2005)

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History of development

Oct. 21, 1947. H. A. McMASTER 2,429,420

CONDUCTIVE COATING FOR GLASS AND METHOD OF APPLICATION

Filed Oct. 5, 1942

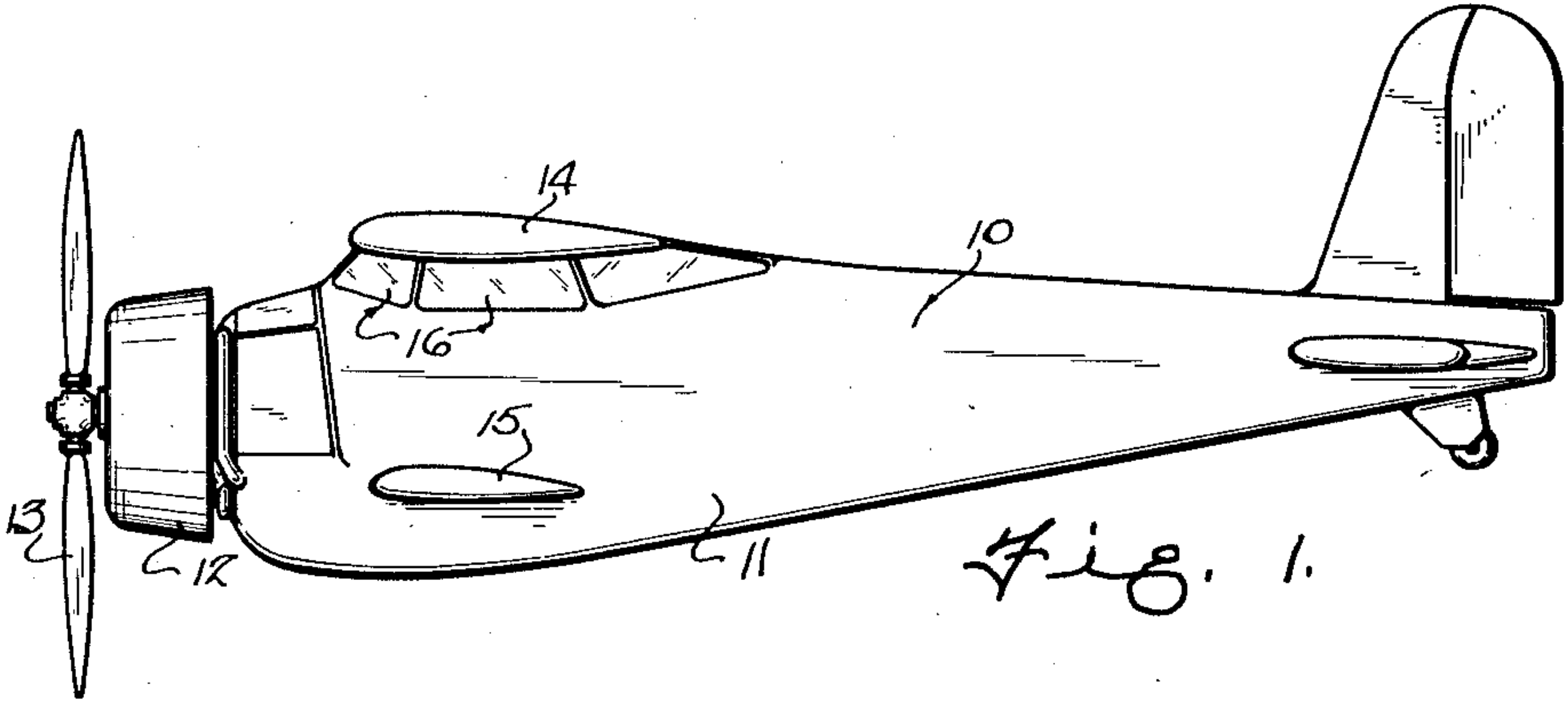

Fig. 1.

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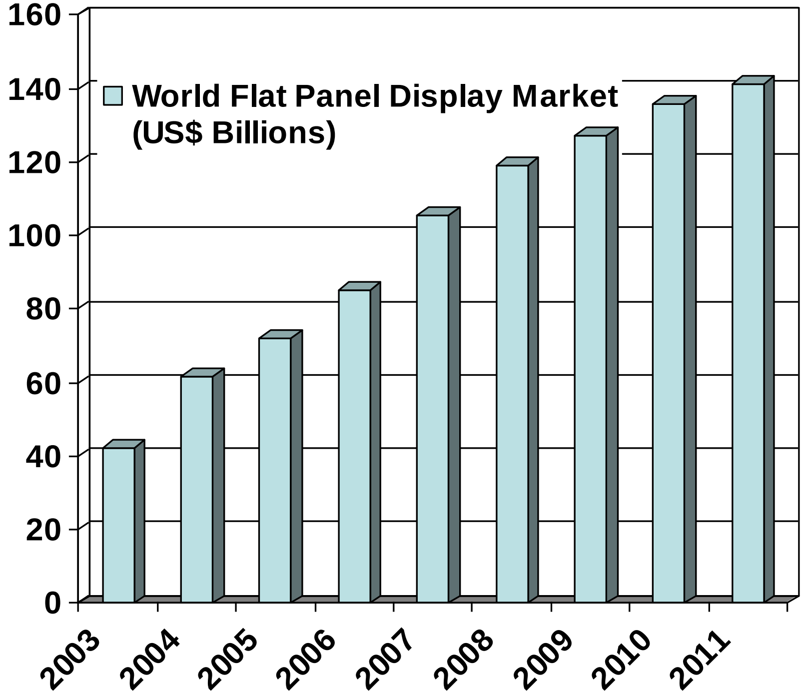
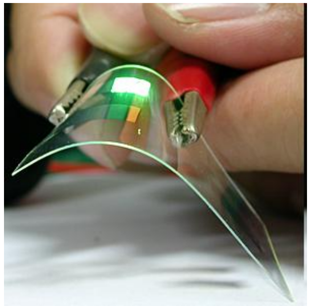
Motivation



German Flat Panel Display Forum



- Transparent conductive oxides (TCOs): key materials in optoelectronics

Present	Rare Indium, etc $$$	+	Toxic	Cd, F, etc
Next generation	Abundant Indium-free $	+	Environmentally friendly	Zn, Ti, Si

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Overview of activities

Transparent conductive oxides
Oxide-based nanocomposites

Elevated temperature
Particle fluxes

Structure
Stoichiometry
Phase composition
Properties

Understanding upper physical limits of performance
Achieving novel nanomaterials

ZnO-based

Wilde, Cornelius (FWIN), Liedke, Vinnichenko

Bilateral, BMWi/AiF, BMBF-TUBITAK

HZB, von Ardenne, GfE Fremat, Bosch, Solayer, Vaciontec, DTF, Heliatek, CreaPhys, Interpane, Euroglas, LIMO, METU, Bilkent Univ.

TiO_2-based

Neubert, Cornelius (FWIN), Vinnichenko

Bilateral, BMBF MatRessource (submitted)

FEP, DTF, Solayer, Vaciontec, LIMO, Euroglas, HZDR Innovation

SiO_x-based

Liedke, Heinig, FWIZ: Friedrich, Schmidt

BMBF-TUBITAK
Abengoa Associated Partnership Agreement

LIMO, METU, Bilkent Univ., Nurol, Abengoa Research

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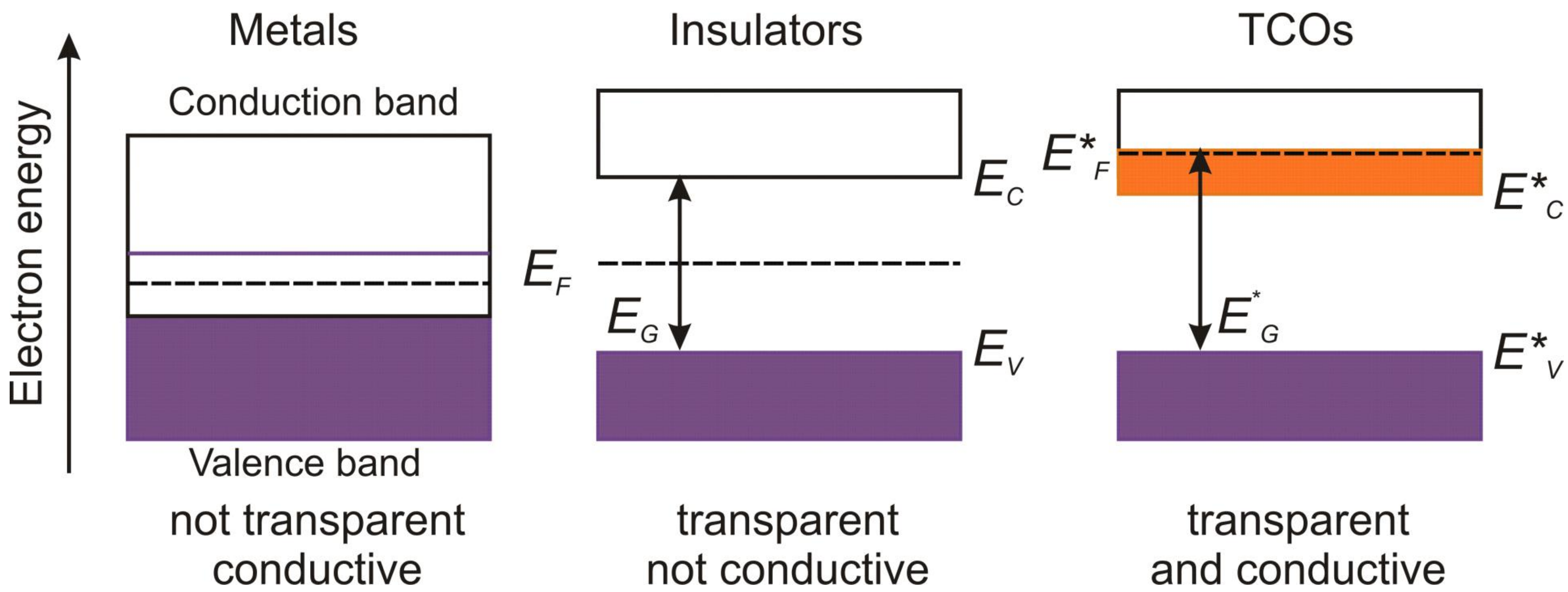
Basics of transparent conductive oxides (TCOs)



Half-empty valence band
Overlapping with
conduction band

Filled valence band
Empty conduction band
Wide band gap E_G>3 eV

Defect-related sub-band
at the bottom of the
conduction band
Wide band gap E_g>3 eV

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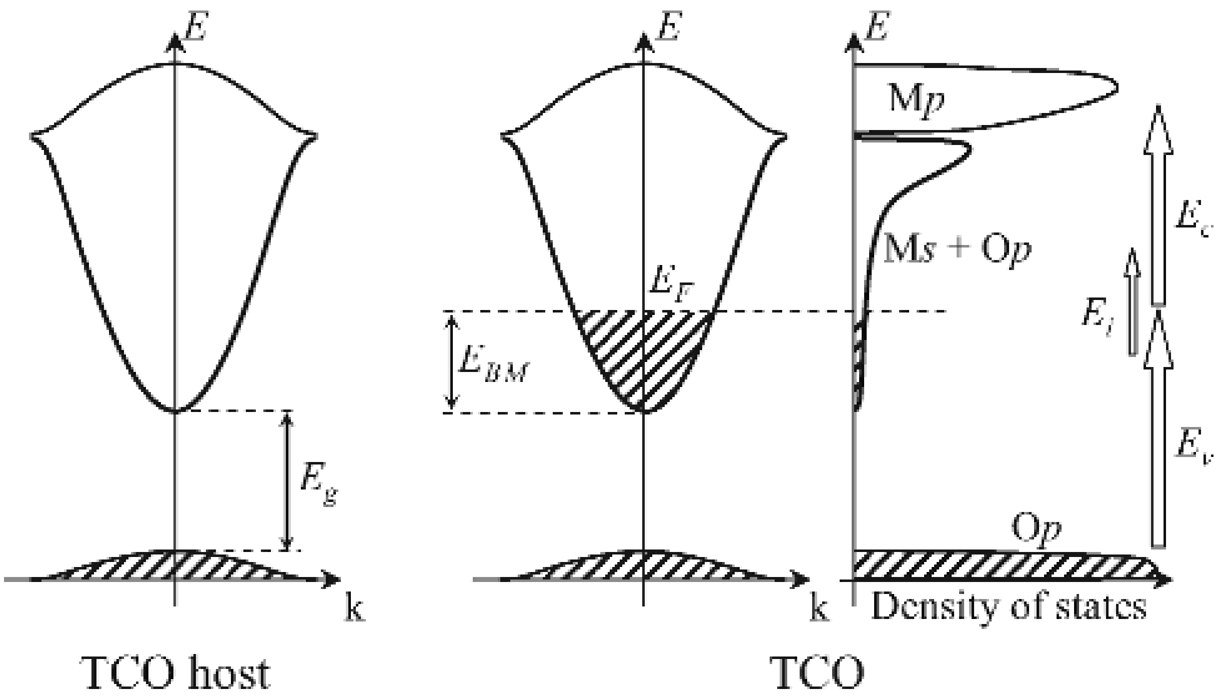
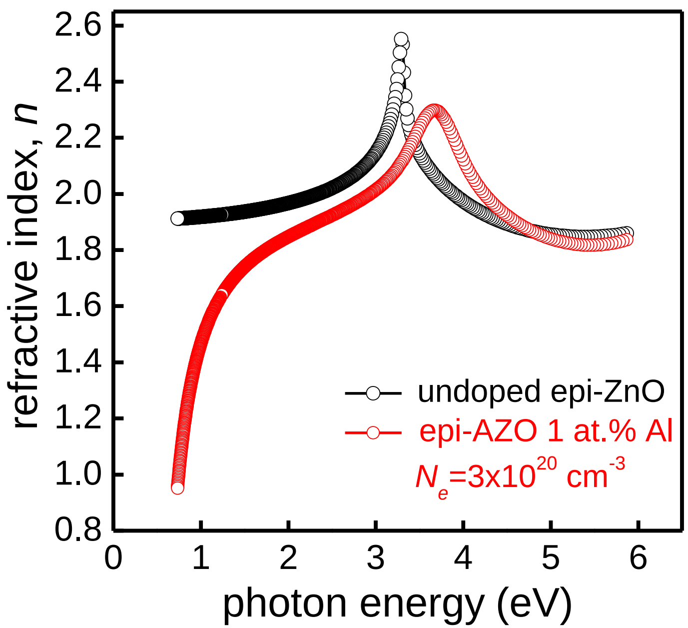
Basics of transparent conductive oxides

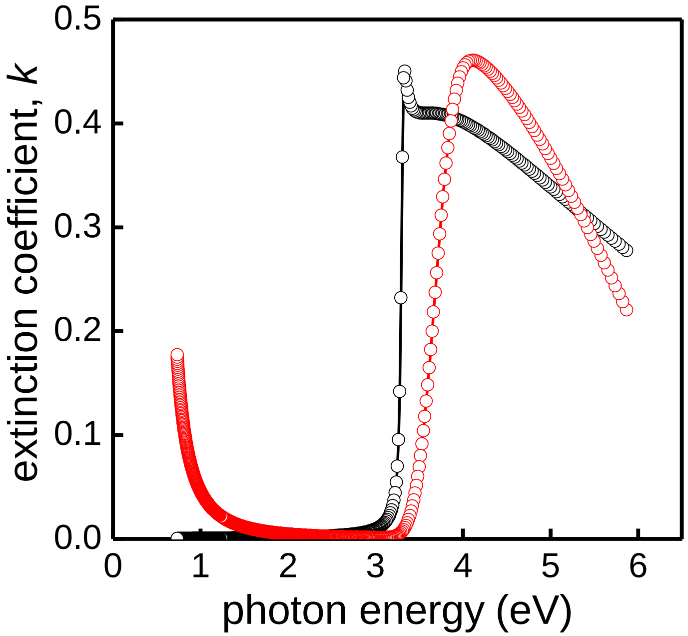


- Material can be highly doped: native defects + extrinsic impurities
- Degenerate n-type semiconductors

Medvedeva in Transparent Electronics: From Synthesis to Applications, Wiley 2010

Basics of transparent conductive oxides





$$\omega_p = \sqrt{\frac{e^2 N_e}{\varepsilon_0 \varepsilon_\infty m^*}}$$

$$\Delta E_G \sim N_e^{2/3}$$

- Photon Energy ≤ $\hbar\omega_p$: free electron absorption in the near IR
- Plasma frequency ω_p ≤ 1 eV

- Photon Energy≥E_G: interband transitions
- Burstein-Moss shift due to free charge carriers

- Nearly metallic electric conductivity: ρ~(1-2)x10^{-4} Ω cm

$$\rho = \frac{1}{e\ N_e \mu_e} = \frac{m^*}{e^2 N_e \tau}$$

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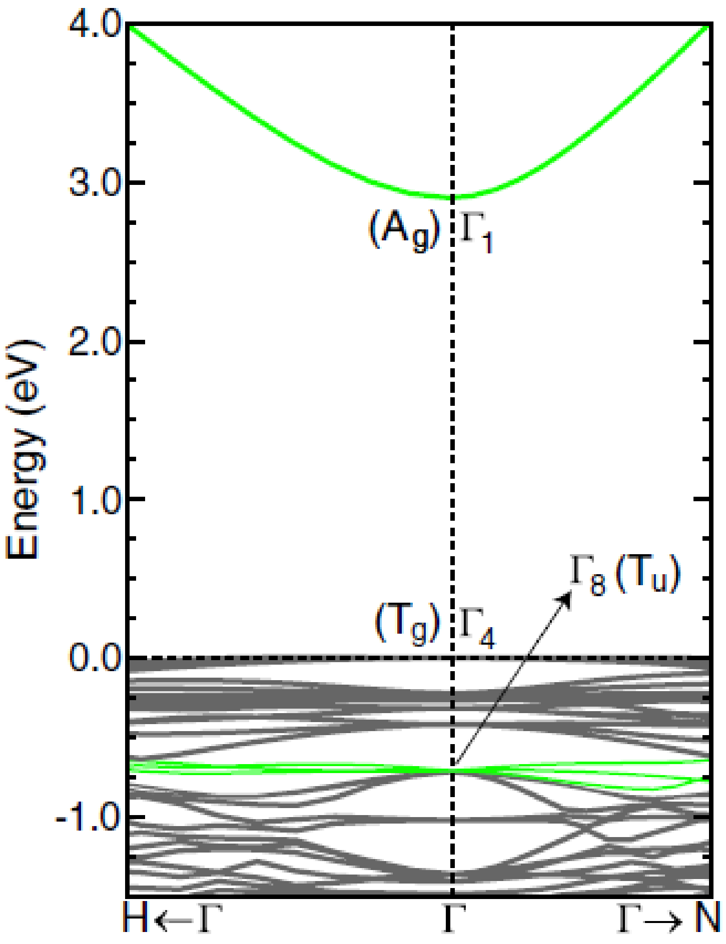
Sn-doped indium oxide (ITO): best understood TCO !?

What is the band gap of In_2O_3?

- Generally accepted: direct gap of E_G=3.75 eV, based on optical investigations
  Hamberg et al, *PRB* 30, 299 (1984)

- X-ray photoelectron spectroscopy: fundamental gap is <3 eV
- In some cases optical data show absorption outset at 2.6 eV
- It is attributed to indirect transitions
  Christou, et al, *JAP* 88, 5180 (2000)
  McGuinness et al, *PRB* 68, 165104 (2003)

- Recent comprehensive study: fundamental band gap is not higher than 2.9 eV, direct gap
- But corresponding transitions are parity forbidden!
- Only transitions from lower levels (green) are allowed



Walsh et al, *PRL* 100, 167402 (2008)

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Basics of transparent conductive oxides

Exclusively post-transition metal oxides?

- CdO, In_2O_3, SnO_2, ZnO-based:
  - $(n\text{-}1)d^{10}ns^2$ electronic configurations
  - four- (ZnO) or six-fold (CdO, In_2O_3, SnO_2) coordinated atoms
  - Conduction band bottom: metal *s* +oxygen *p*
- TiO_2-based: exception

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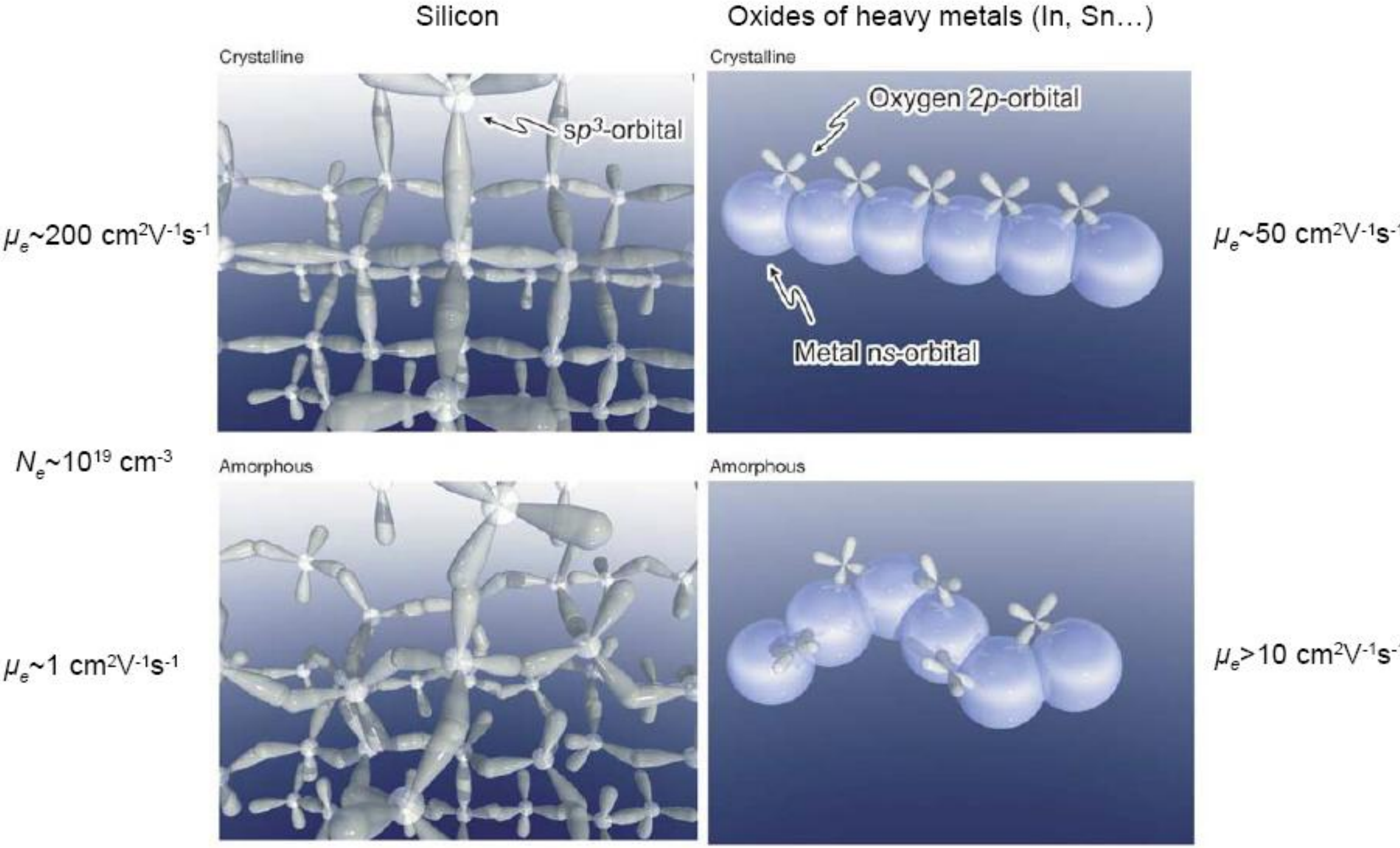
Basics of transparent conductive oxides



Nomura et al, *Nature* 432, 488 (2004)

- Not true for TiO_2-based TCOs!

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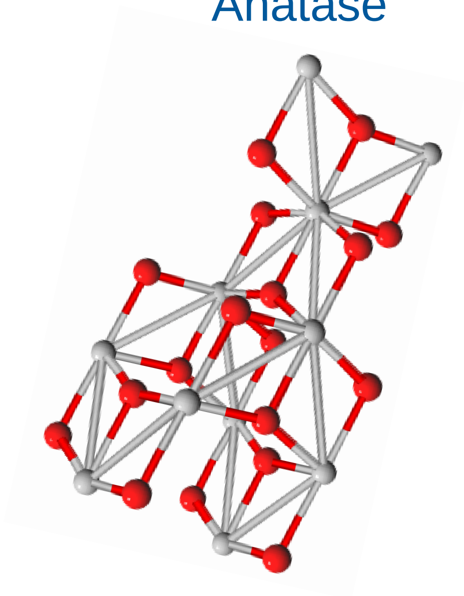
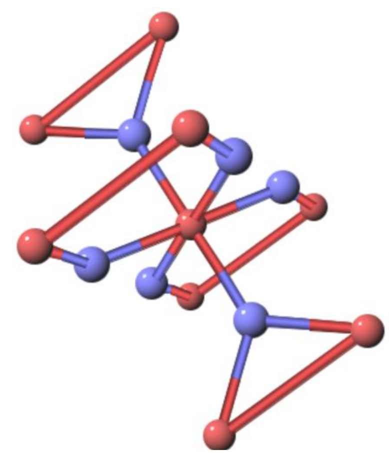
Basics of transparent conductive oxides: TiO_2:Nb/Ta

- Difference to conventional transparent conducting oxides (TCOs):
  - Conduction band bottom:
    - no extended metal s-states
    - mainly formed by Ti *3d* orbitals
  - Different phases/polymorphs – different electrical properties:
    - Amorphous: non-conductive
    - Anatase: very well conductive (low m*)
    - Rutile: only weak conductivity (high m*)
  - High refractive index
  - By now highest quality films are achievable only using epitaxial substrates

Anatase



Rutile



- Challenges:
  - introducing controllable oxygen deficiency into the material
  - control of the phase composition
  - achieving high quality polycrystalline films

Hitosugi et al, Phys.Stat.Sol (a) 207, 1529 (2010)

http://cst-www.nrl.navy.mil

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Basics of transparent conductive oxides: TiO_2:Nb/Ta

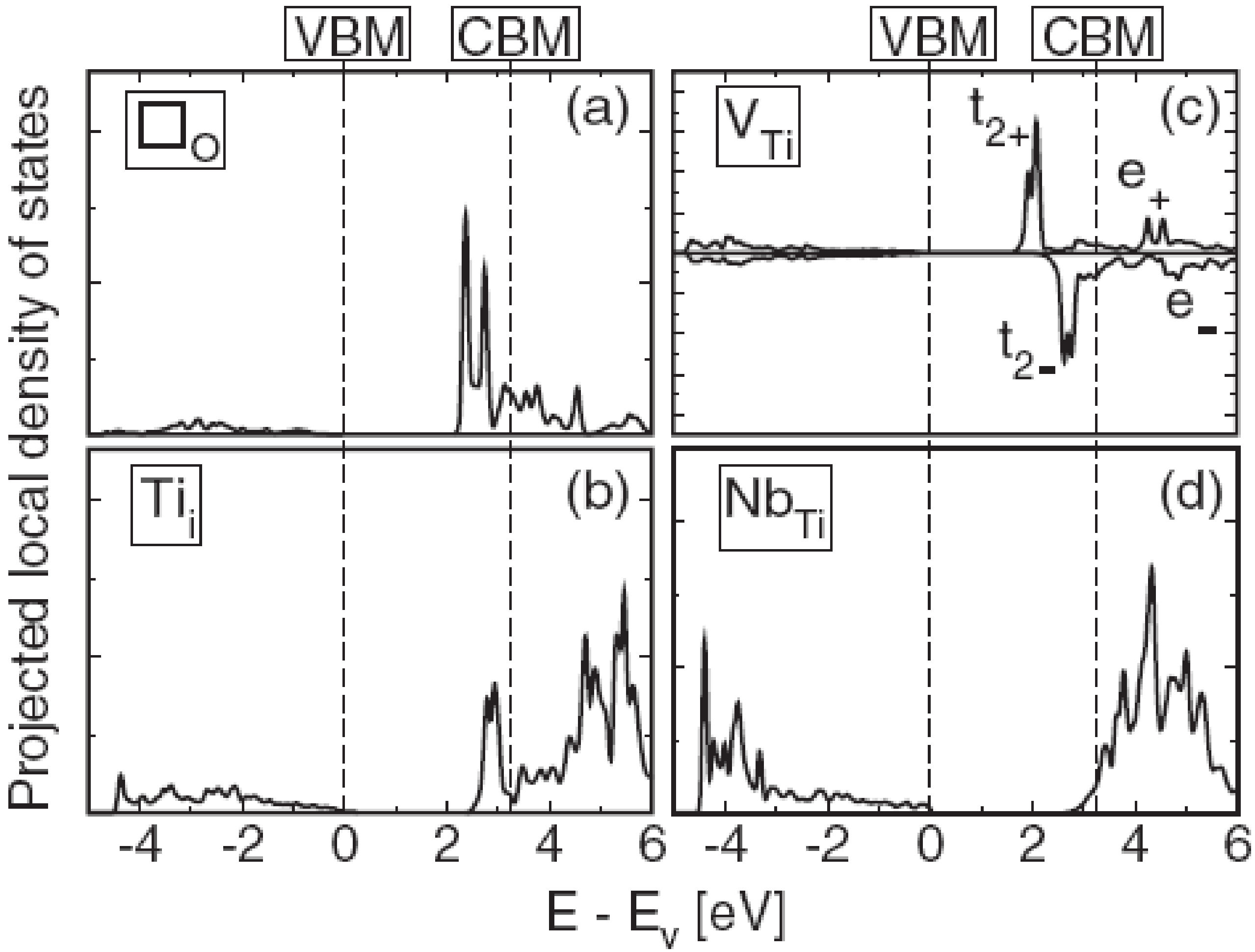

FIG. 4. Calculated local density of states (DOS) for $\Box_O^0$, Ti_i^0, V_{Ti}^0, and Nb_{Ti}^0 using GGA. The hosts VBM and CBM are indicated by vertical-dashed lines.

Osorio-Guillen, Lany, Zunger, Phys.Rev.Lett. 100, 036601 (2008)

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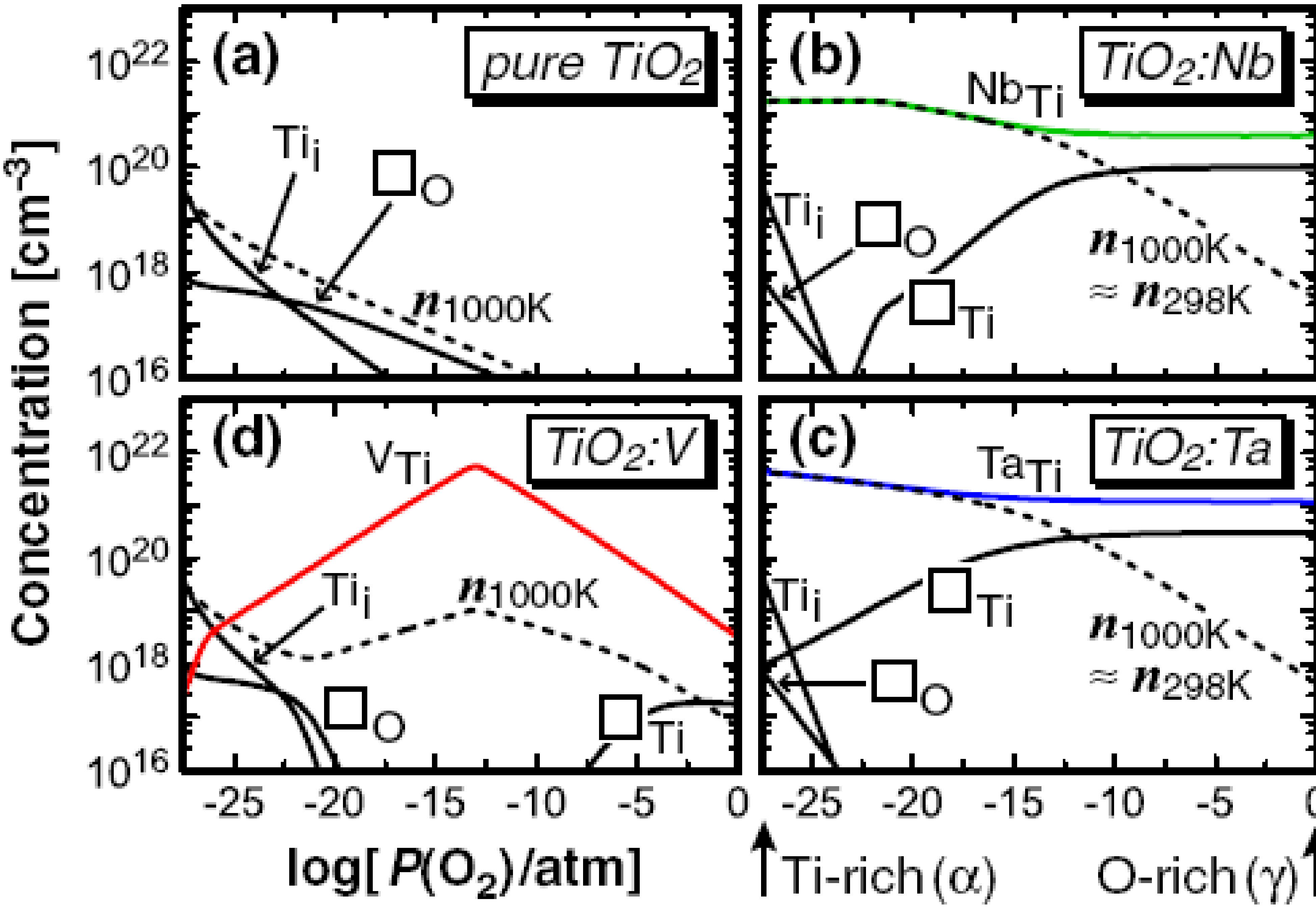
Basics of transparent conductive oxides: TiO_2:Nb/Ta



Osorio-Guillen, Lany, Zunger, Phys.Rev.Lett. 100, 036601 (2008)

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Challenges and Objectives

"… *understanding of the basic physics and chemistry of metal oxide surfaces lags a decade or more behind that of metals and semiconductors*…"

Henrich and Cox, The Surface Science of Metal Oxides, Cambridge University Press, 2000

- Understanding even of the properties of metal oxide films and single crystals often lags behind
- Basic understanding:
  - Defect formation
  - Incorporation and electrical activation of doping impurity
  - Formation of secondary phases and their properties
  - Limits to the charge carrier transport
- Controllability and reproducibility:
  - Fine tuning of the metal/oxygen flux
  - Understanding role of the plasma energetic species
  - Thin film microstructure and surface morphology
- Addressing these issues is crucial to ensure further progress

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Experimental approach: film synthesis

- Four sputter deposition systems
- DC and pulsed magnetron sputtering
  - Reactive (Ar + O_2), metallic (elemental and alloy) targets
  - Non-reactive (Ar), conductive (reduced) ceramic targets
- 2- and 3-inch magnetrons, balanced and unbalanced
- Energy-resolved mass spectrometry for detection of plasma ion species
- Langmuir probe with fine time resolution
- Precise tuning of metal/oxygen flux ratio:
  - Zn, Zn-Al, Zn-Ga: magnetron voltage
  - Ti, Ti-Nb: magnetron current
  - Reduced ceramic targets: optical emission of plasma intensity as a feedback

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Experimental approach: film characterization

- Annealing chamber (vacuum, Ar, O_2), equipped with in situ four point probe for resistivity measurements
- Annealing unit is transferrable to other experimental set-up: e.g. in situ XANES
- In situ spectroscopic ellipsometers: M-2000V, M-2000FI, J.A. Woollam Inc.
- Spectral photometer: SoliSpec 3700, Shimadzu

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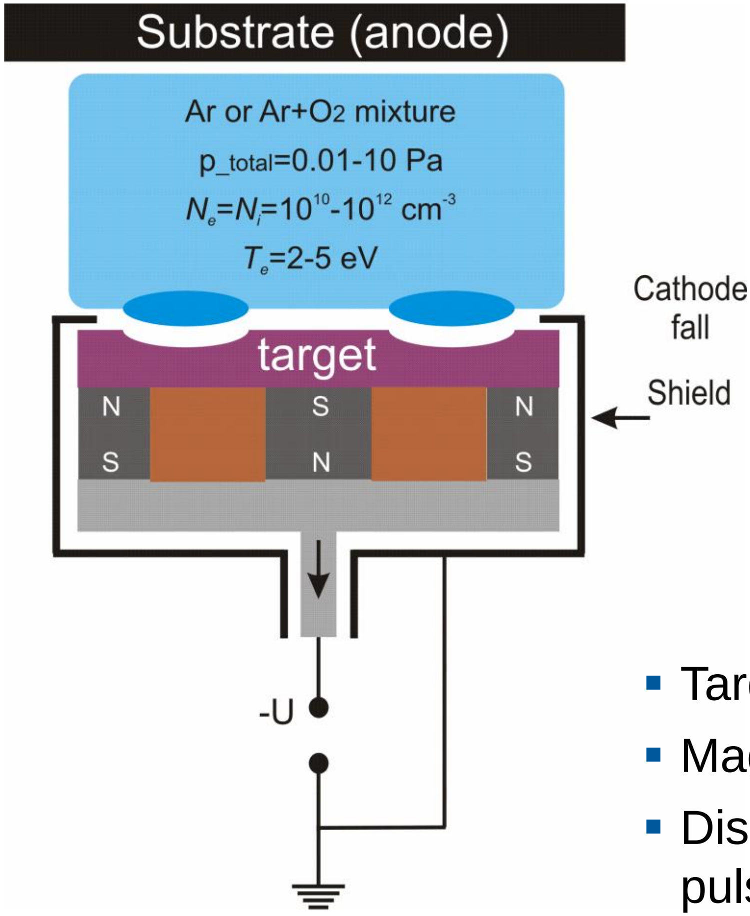
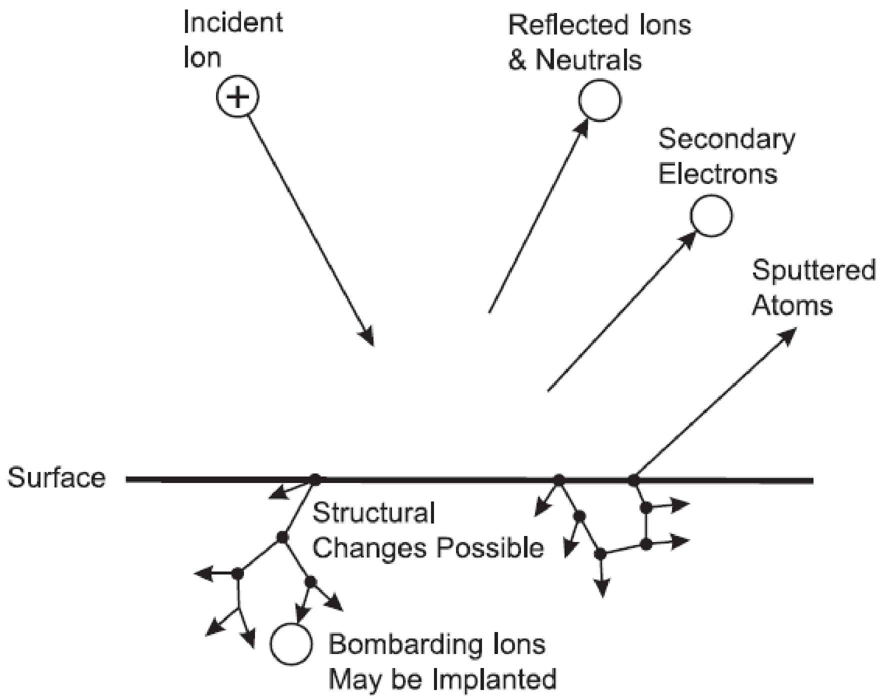
Basics of magnetron sputtering





Ellmer, *JPD* 33, R17 (2000)

- Targets: metallic or compound
- Magnetic field configuration: balanced or unbalanced
- Discharge modes: DC, medium-frequency (MF) pulsed, RF
- Energetic particle bombardment during growth may be used as a tool to affect the film structure and properties

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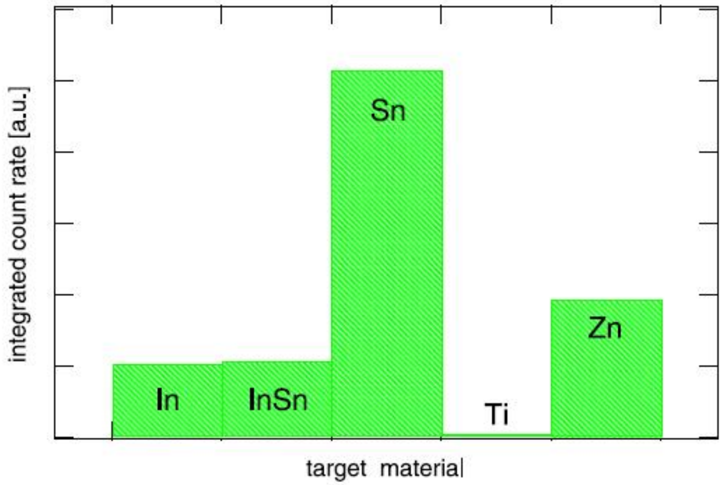
Role of energetic particles

ZnO:Al

Energetic negative ions

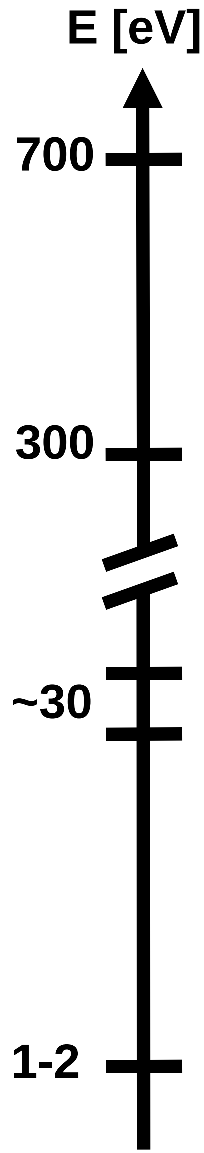


Ellmer, Welzel, *JMR* **27** (2012)

Ge
de
→
000)
985)

Some ion assistance increases adatom mobility → better films

Mendelsberg et.al., *J. Phys. D* **44** (2011)
Anders, *APL* **80** (2010)



Typical highest energies in DC magnetron sputtering (=qV_T)

displacement energy: O

displacement energy: Zn

Look et.al., *APL* **75** (1999)
Redondo-Cubero, Vinnichenko, Krause et al *JAP* **110** (2011)

Activation of defect annealing

S.J. Zwinkle and C. Kinoshita, J. Nucl. Mater. **251** (1997)

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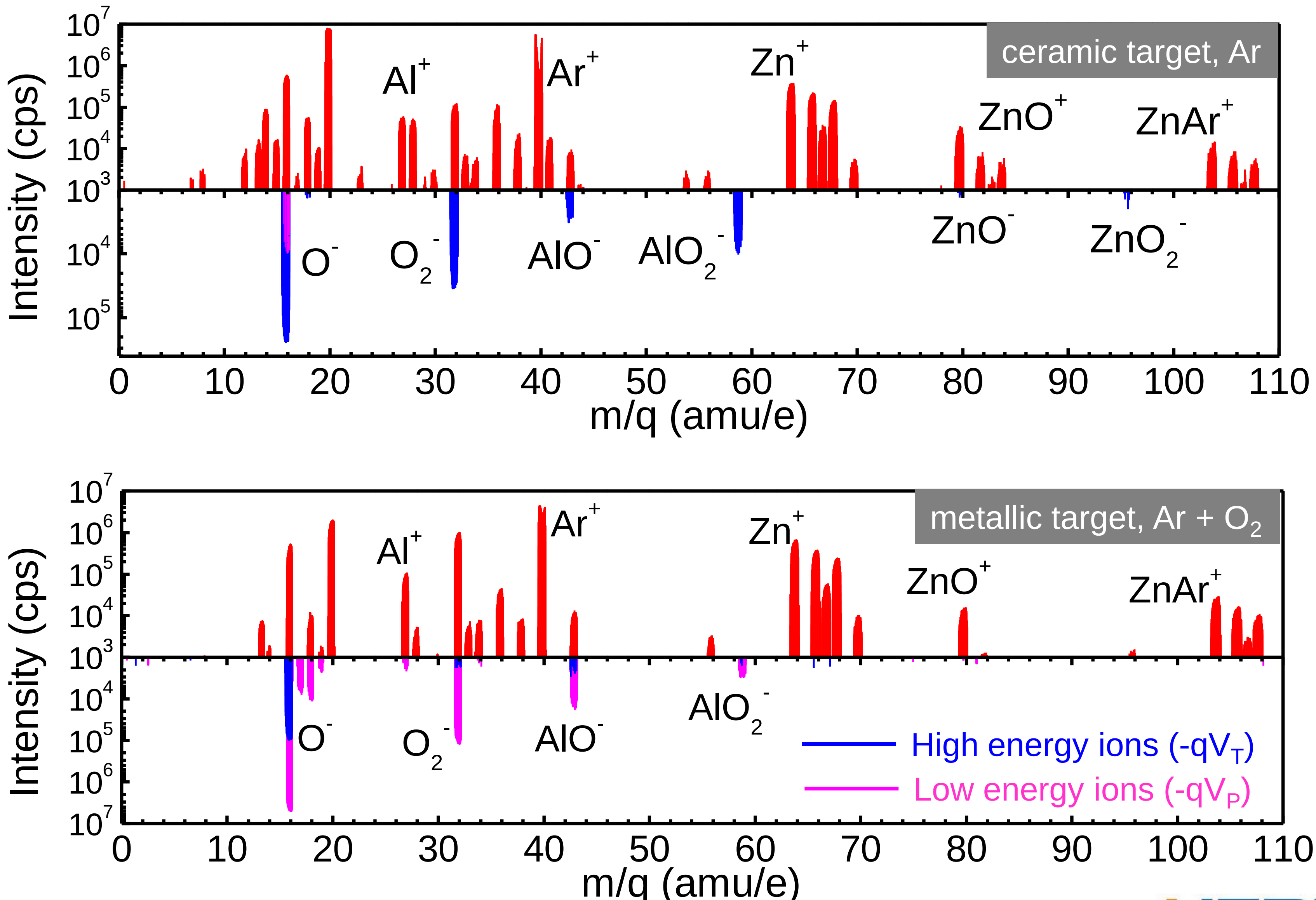
Metallic vs ceramic targets: plasma



C. Wilde (in preparation)

Direct growth, reactive magnetron sputtering, variation of deposition temperature

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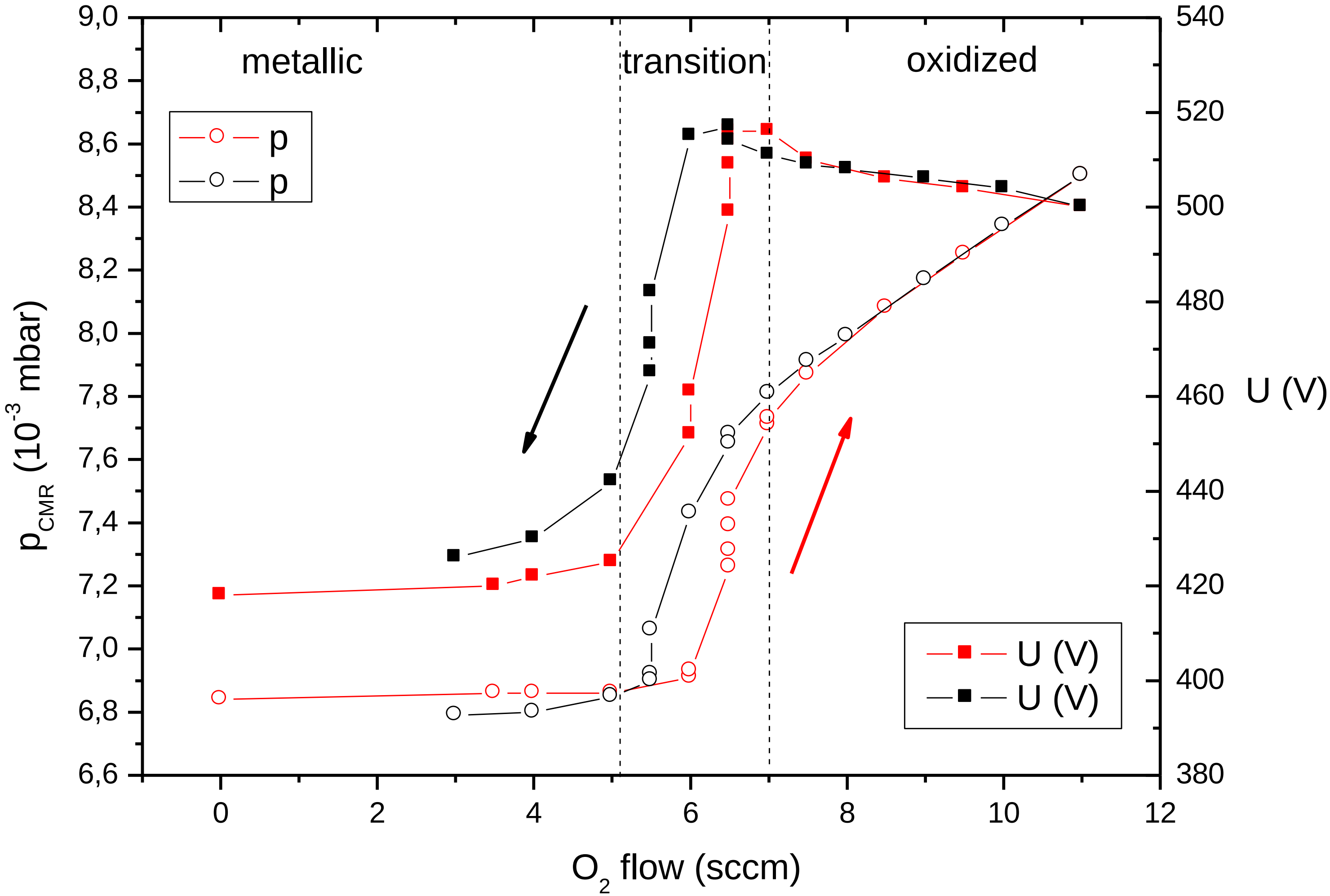
Reactive sputtering: hysteresis

TiO_2

pressure-voltage vs. flow hysteresis of Ti in (Ar,O_2) , P=500W



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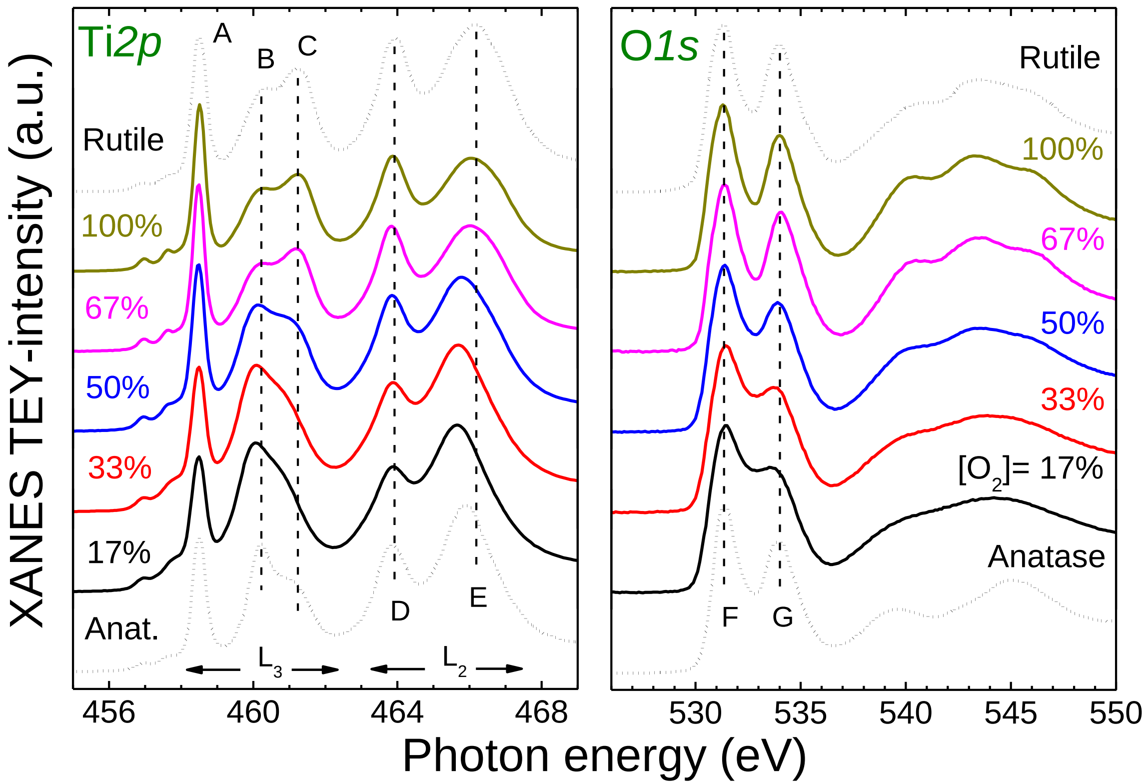
Local atom arrangements

TiO_2

XANES data

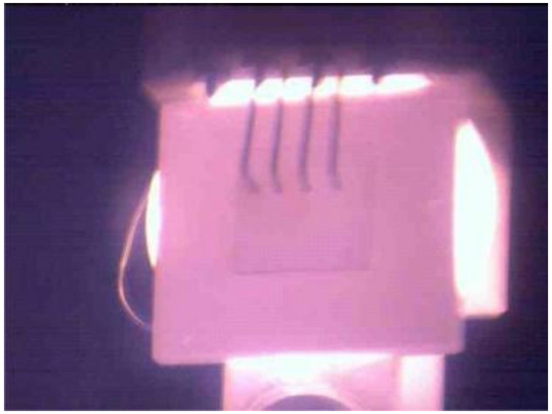


- Ti2p spectra: 2p to 3d transitions
- $L_{3,2}$ edges: spin-orbit splitting of Ti-2p core level into $2p_{3/2}$ and $2p_{1/2}$
- XANES shows differences between as-grown disordered anatase- and rutile-like films, which are indistinguishable by XRD

Gago, Vinnichenko et al. *Plasma Process. Polym.* 7, 813 (2010)

Two-step process, DC magnetron sputtering of reduced ceramic targets

deposition of amorphous film
(no heating)
reduced ceramic target



vacuum annealing at ~400°C, 1 hour

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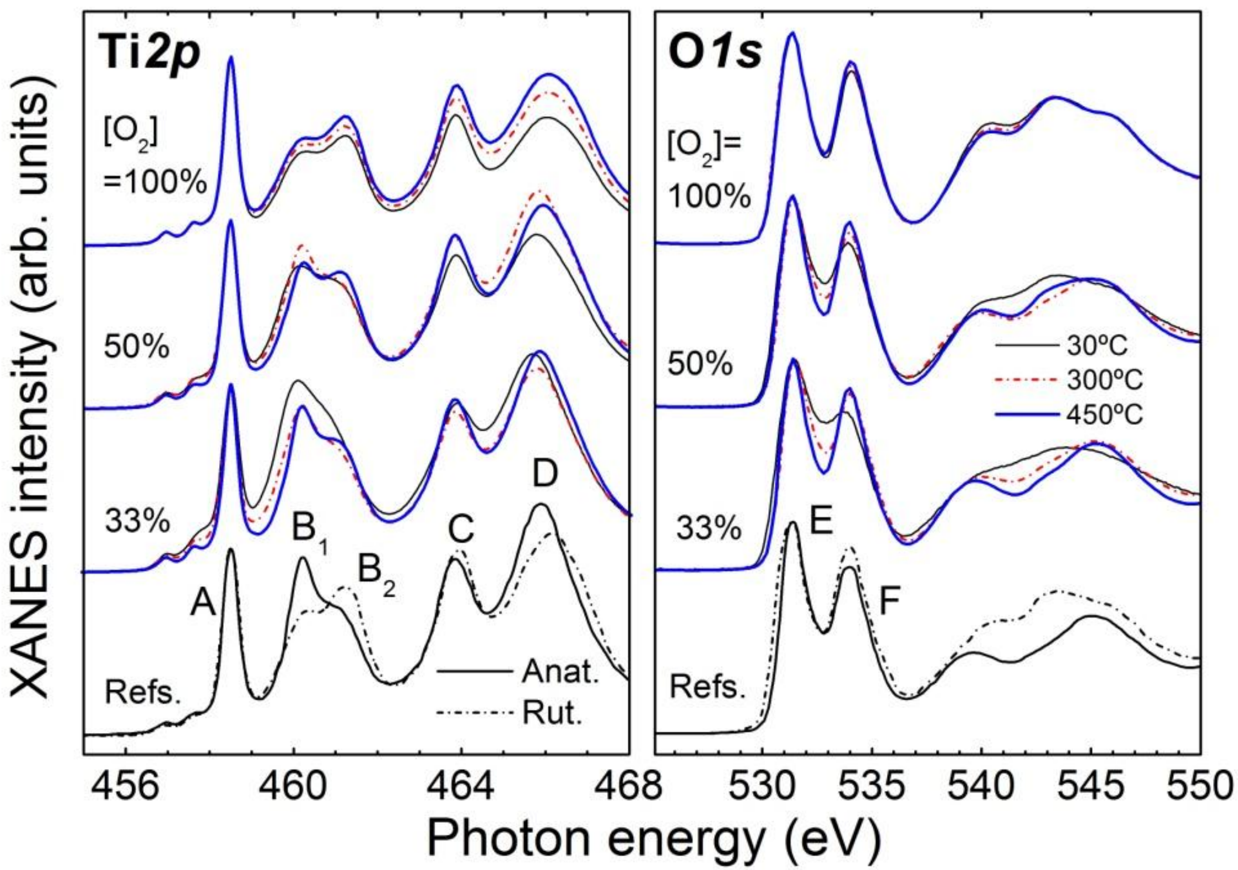
Local atom arrangements

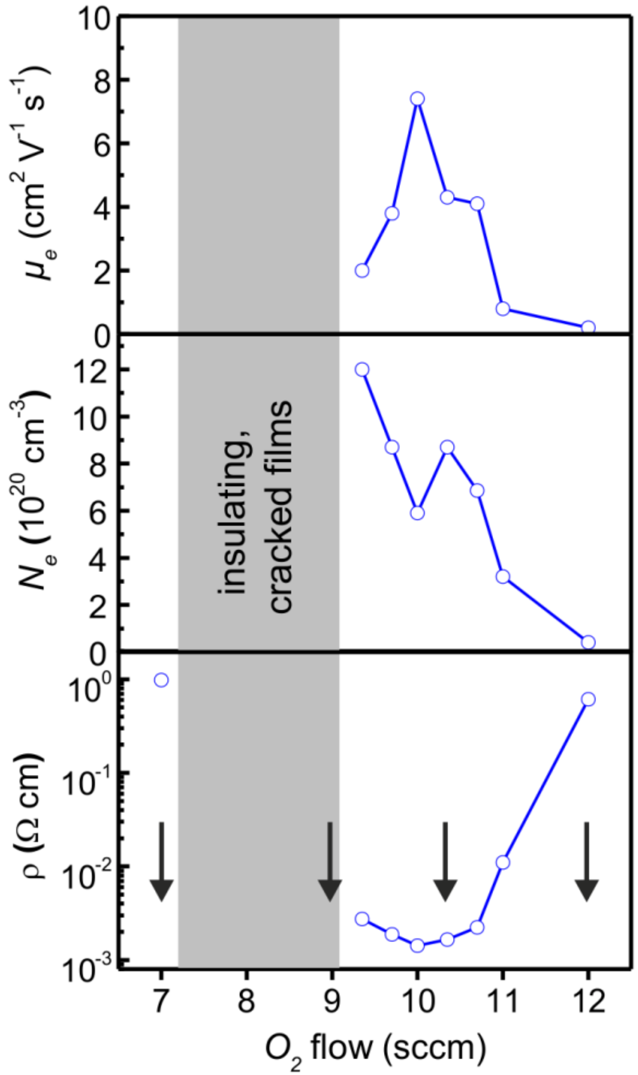
XANES data

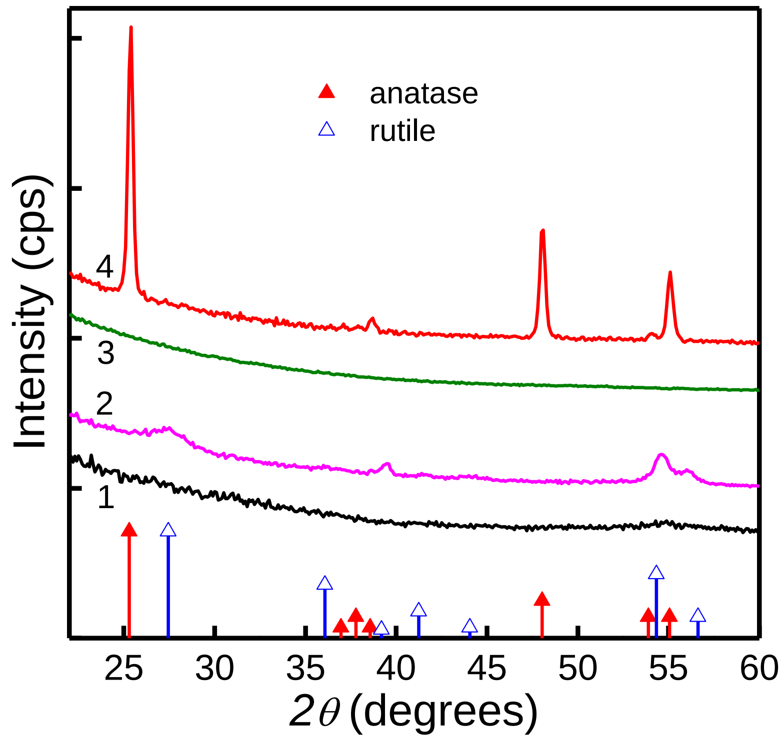


- Amorphous anatase-like films readily crystallize in good polycrystalline anatase TiO_2
- Disordered nc-rutile TiO_2 films remain stable upon annealing

Gago, Redondo-Cubero, Vinnichenko, Vazquez, *Chem.Phys.Lett.* 511, 367 (2011)

Relation to the structure and properties





- 1: as deposited (O_2 flow 9 sccm)
- 2: the same films after annealing in vacuum
- 3: as deposited (O_2 flow 10.35 sccm):
- 2: the same films after annealing in vacuum

Vinnichenko et al (in preparation)

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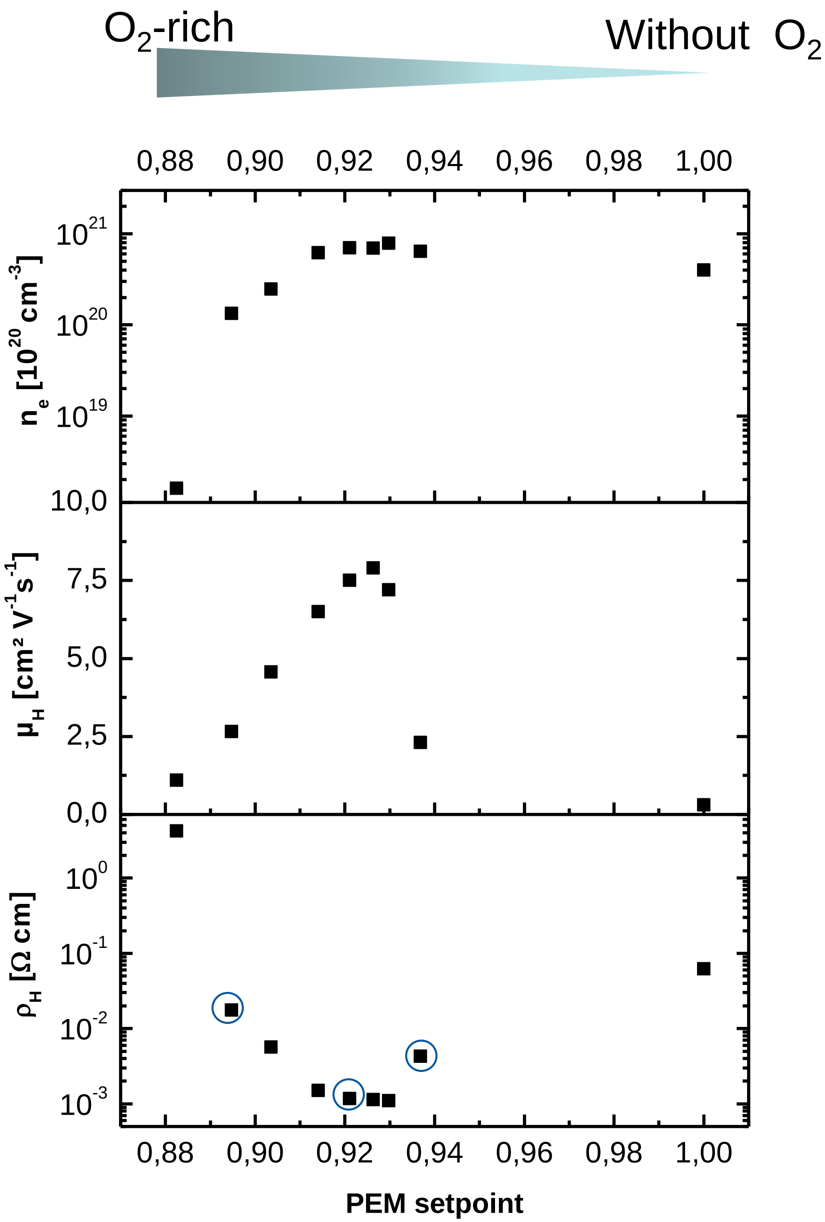
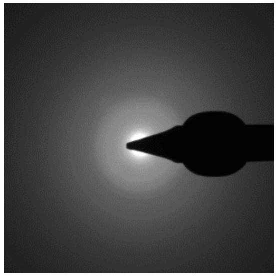
TiO_2:Ta: structure and properties

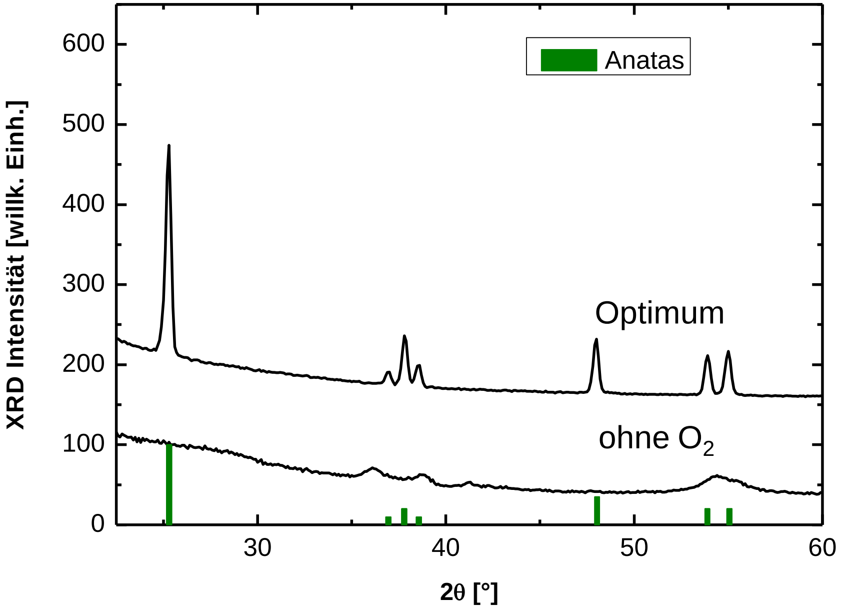


As-deposited

- insulating
- XRD-amorph.
- TEM-amorph.



Annealed



Neubert et al (in preparation)

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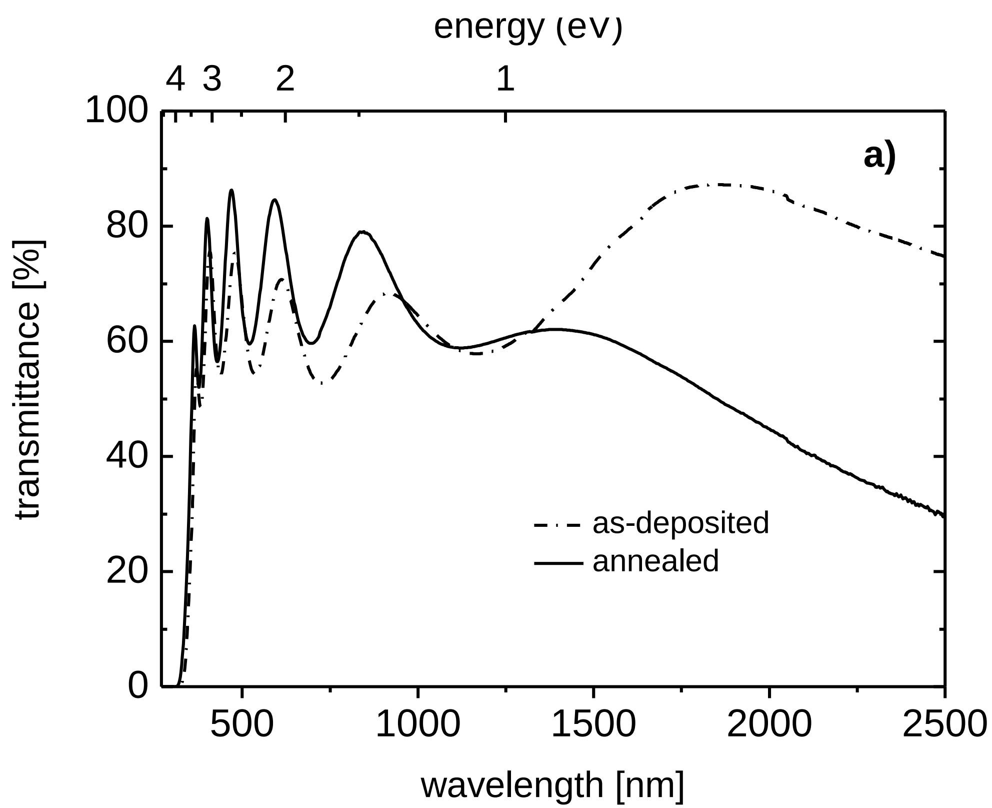
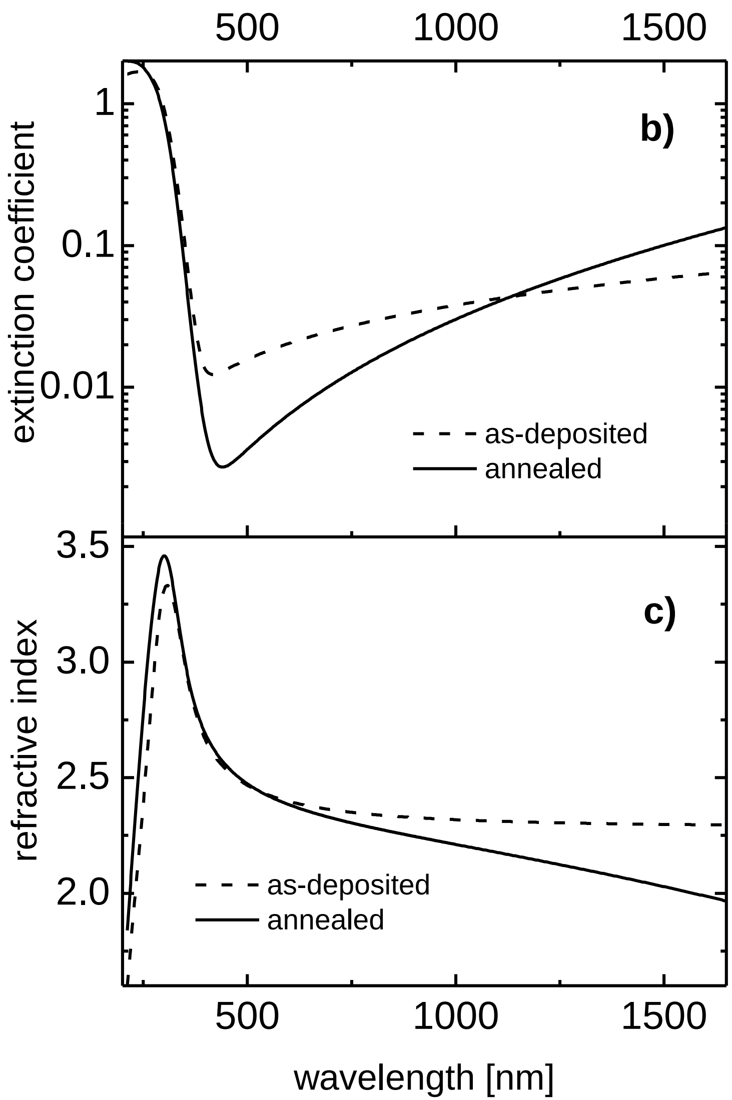
TiO_2:Ta: optical properties, optimized films





Neubert et al (in preparation)

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Summary

- The polycrystalline anatase TiO_2-based films with properties above current state of the art are realized by magnetron sputtering

- High-precision control of the oxygen deficiency and prevention of the rutile seed layer formation are crucial

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