FIRST-PRINCIPLES MODELLING OF DOPANTS AT INTERFACES IN TCO MATERIALS

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Workshop „Transparente und flexible Elektronik“
Universität Leipzig, 28. September 2010

$$\underline{\sigma} = \underline{\sigma}(\underline{\varepsilon})$$

$$m_i \, \ddot{x}_i = f_i$$

$$\hat{H} \, \Psi = E \, \Psi$$

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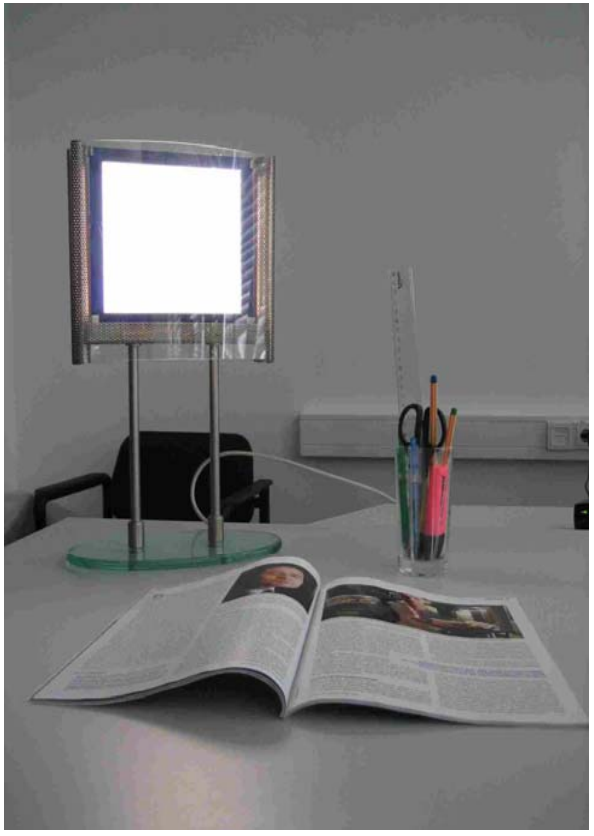
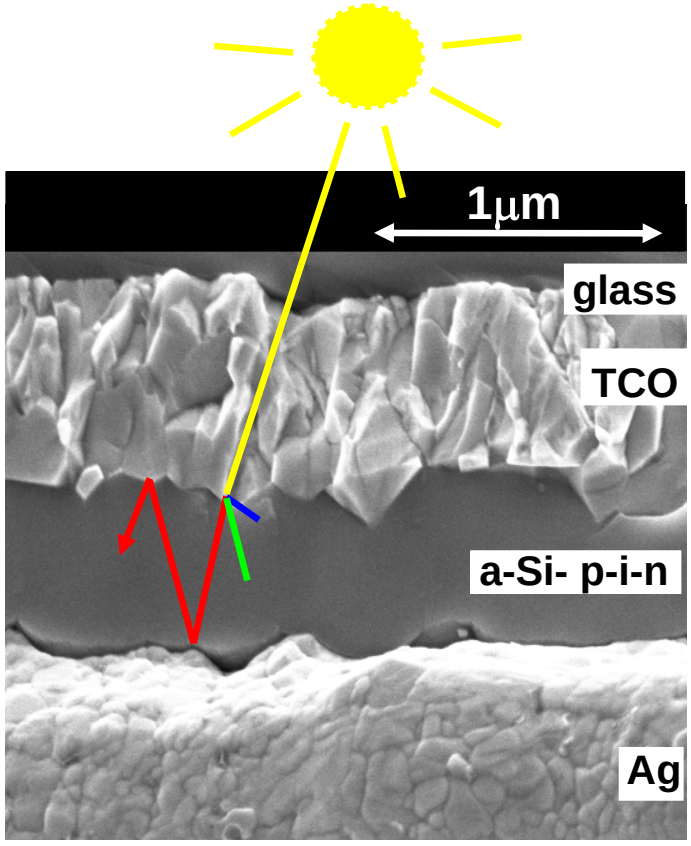
First-principles DFT study of dopant elements at grain boundaries in the TCO materials ZnO and TiO_2

Wolfgang Körner and Christian Elsässer, Fraunhofer IWM





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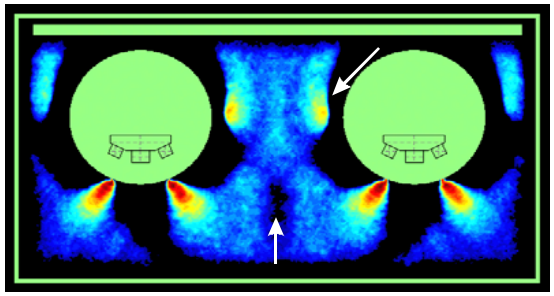
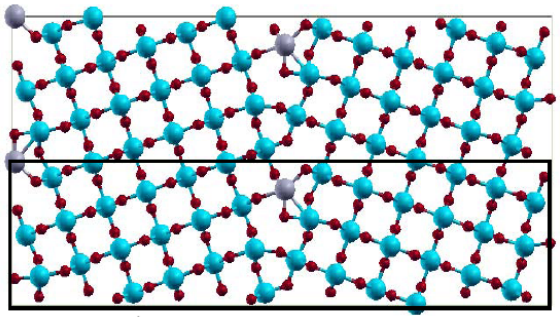
METCO – a Multidisciplinary Effort towards advanced Transparent and Conducting Oxide electrodes





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http://www.transparente-elektroden.de/

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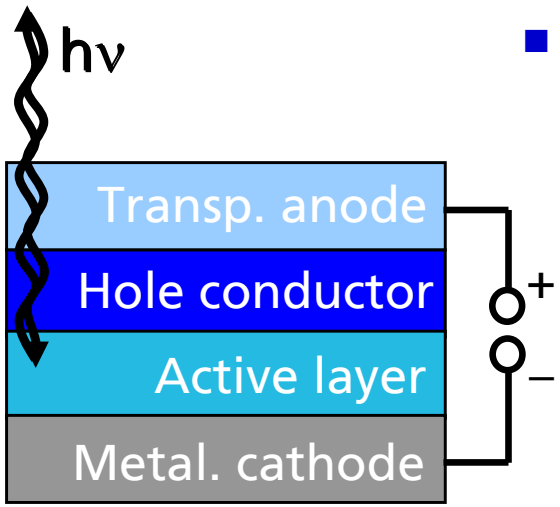
Transparent and conductive oxide thin-film systems



- need: large-area electrical contacts for solar cells and light emitting diodes
- demands:
  - high optical transmittance and electrical conductance
  - proper matching of band structures at interfaces
  - sufficient light scattering for thin-film solar cells
  - capability for patterning and processing
  - low-cost film deposition on large areas
- desire: p-doping … p-n hetero-junctions … transparent electronics

ZnO

- TCO: transparent and conducting oxide **ZnO:X (X = N, P, Al, Ga)**
  - alternative material to ITO
  - large-area thin-film top electrode for solar cells or OLED devices
  - polycrystalline microstructure
    - **interaction of dopants with grain boundaries**
- DFT: density functional theory
  - LDA: local density approximation, for optimisation of atomic structures
    - **formation energies** of structural defects
  - SIC: self interaction correction, for analysis of electronic structures
    - **defect levels** in energy gap of more accurate band structure
  - supercell models, **m**ixed **b**asis, **p**seudo**p**otentials (MBPP code)

First-principles Density Functional Theory
Mixed-basis pseudopotential method

Meyer, Elsässer, Lechermann, Fähnle, et al. (origin: MPI-MF Stuttgart)

density functional theory	LDA, GGA … SIC-LDA, LDA+U …
translational lattice symmetry	periodic supercell models
core-valence interactions	norm-conserving pseudopotentials
valence electrons	plane waves and localized orbitals

⇒ output: energies and forces
crystal structures, defect configurations
electronic structure, chemical bonding
phase stabilities, defect energies

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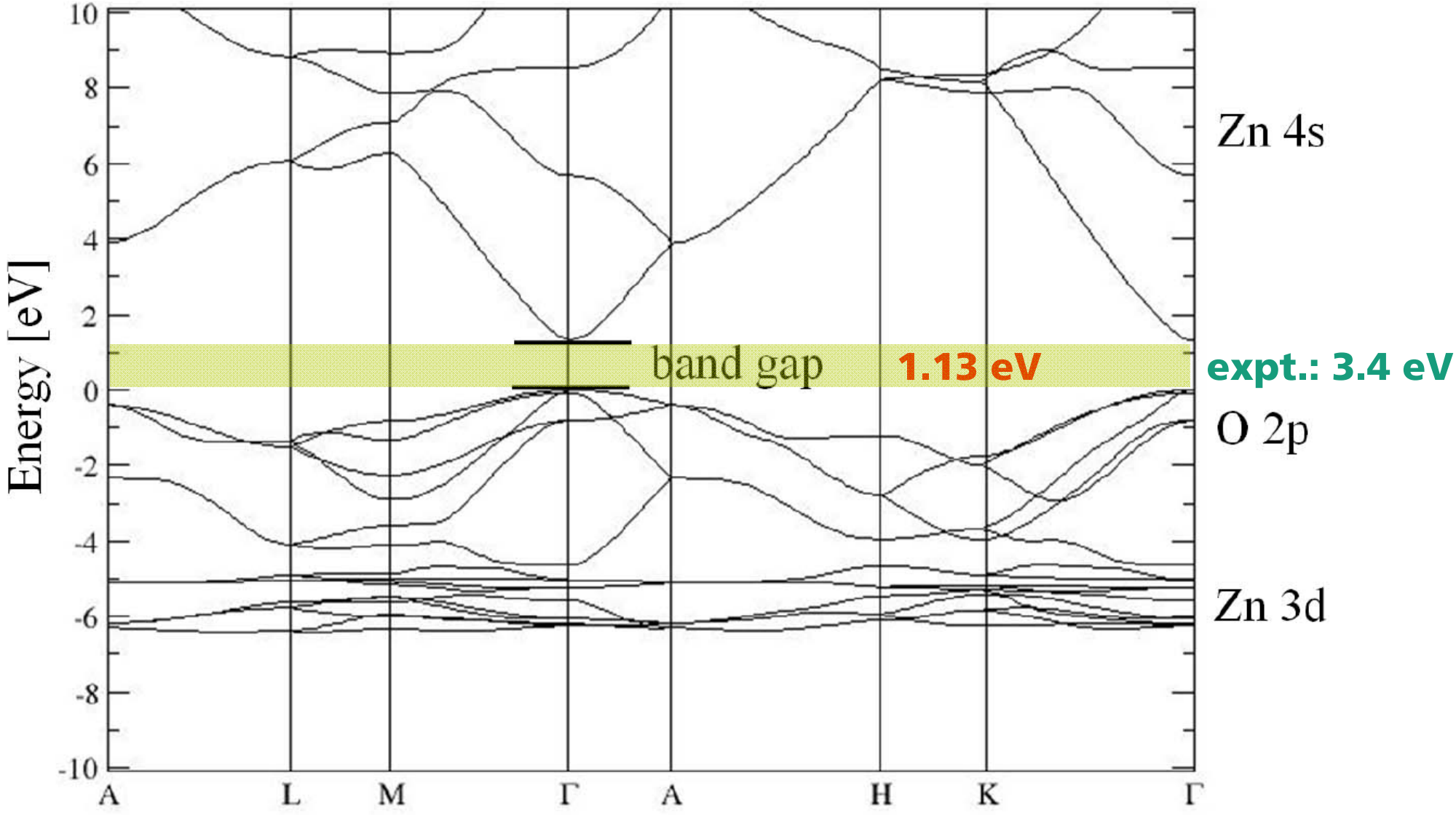
Band structure of bulk ZnO – LDA



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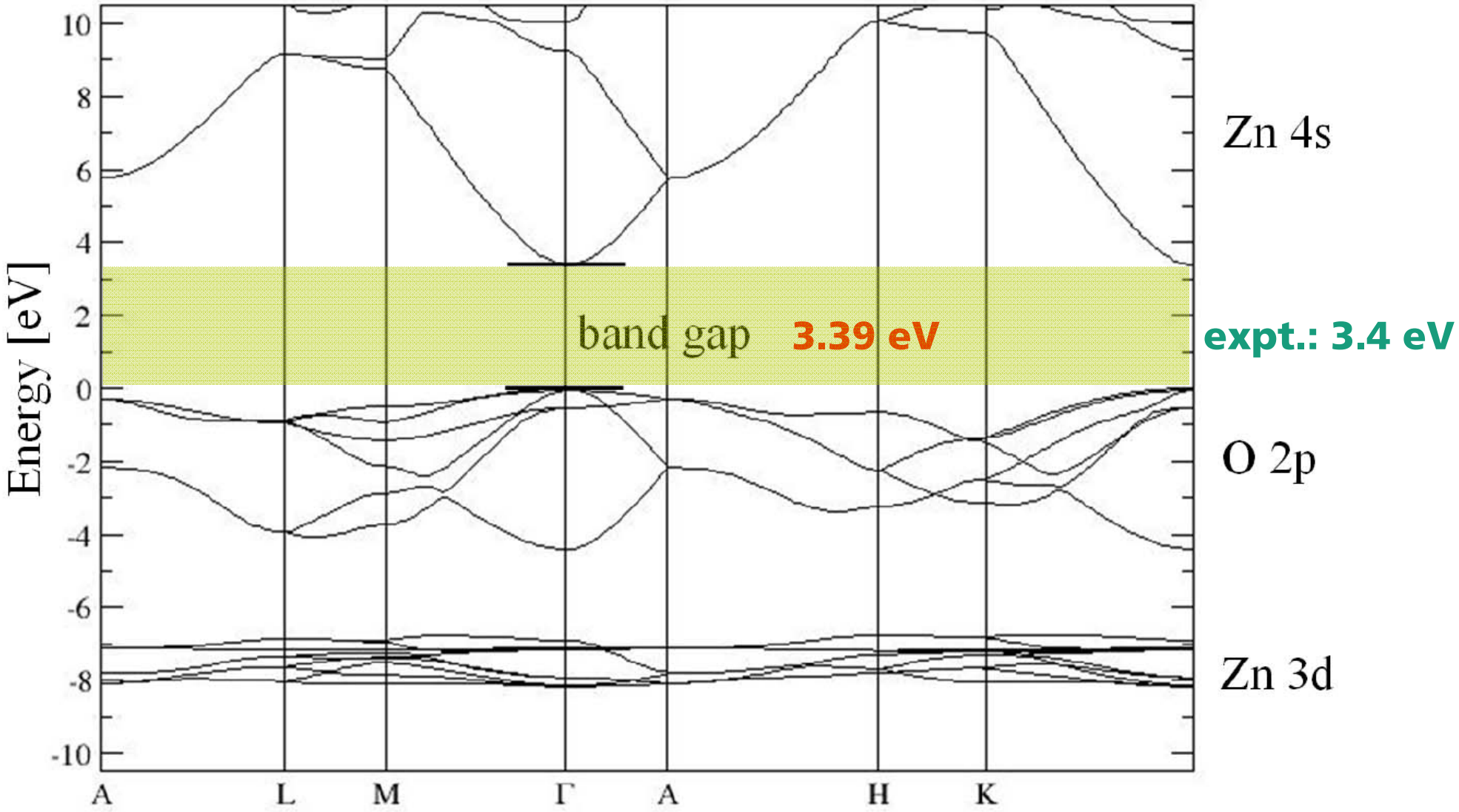
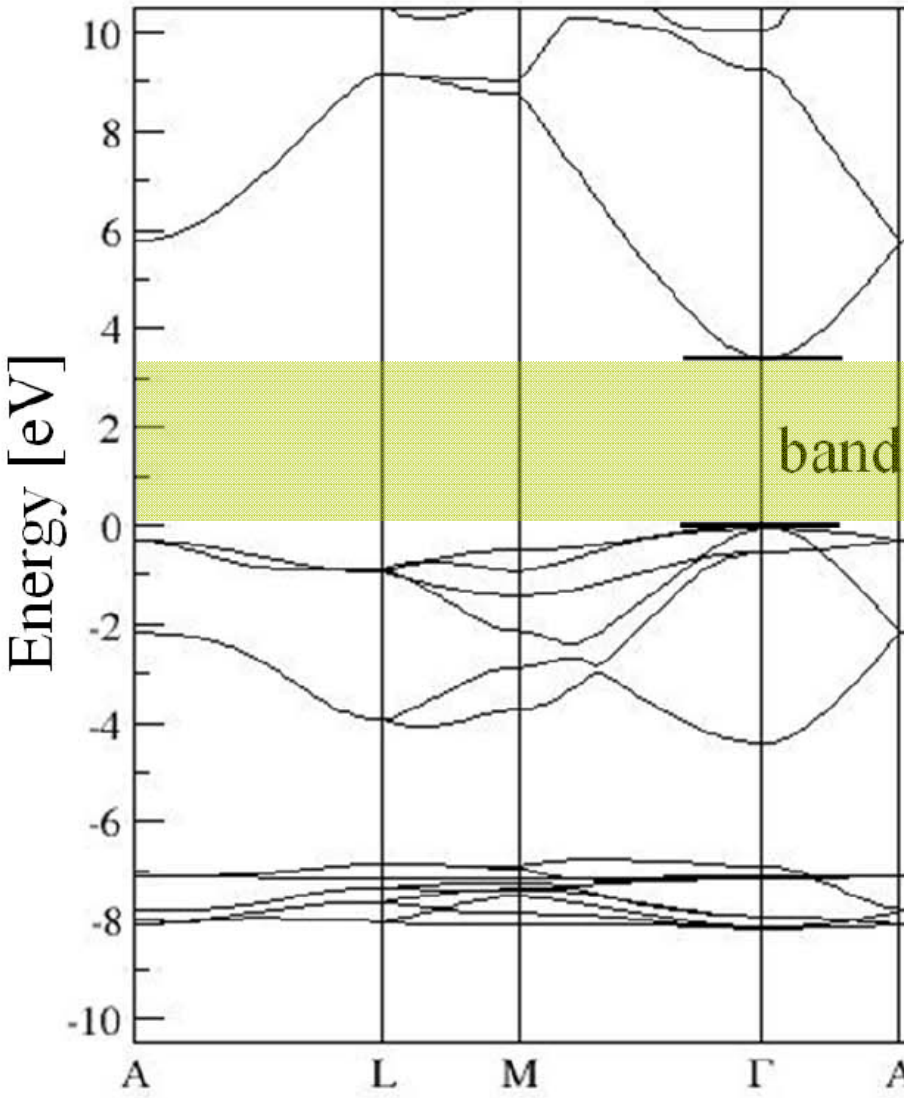
Band structure of bulk ZnO – SIC



bulk SIC: **Zn-3d** 100%, **O-2s** 100%, **O-2p** 80%, $\alpha = 0.8$

Band structure of bulk ZnO – SIC



- formalism: **SIC pseudopotentials**

  cf. Vogel, Krüger, Pollmann
  Phys. Rev. B 54 (1996) 5495

$$\Big(-\nabla^2 + V_l + V_{\mathrm{H}}[n_v] + V_{\mathrm{xc}}[n_v] \underbrace{- w_l \Big[V_{\mathrm{H}}[n_l] + V_{\mathrm{xc}}[n_l]\Big]}_{:=-V_{\mathrm{cor}}[n_l]}\Big)\Psi_l^{pp} = \epsilon_l^{pp}\Psi_l^{pp}$$

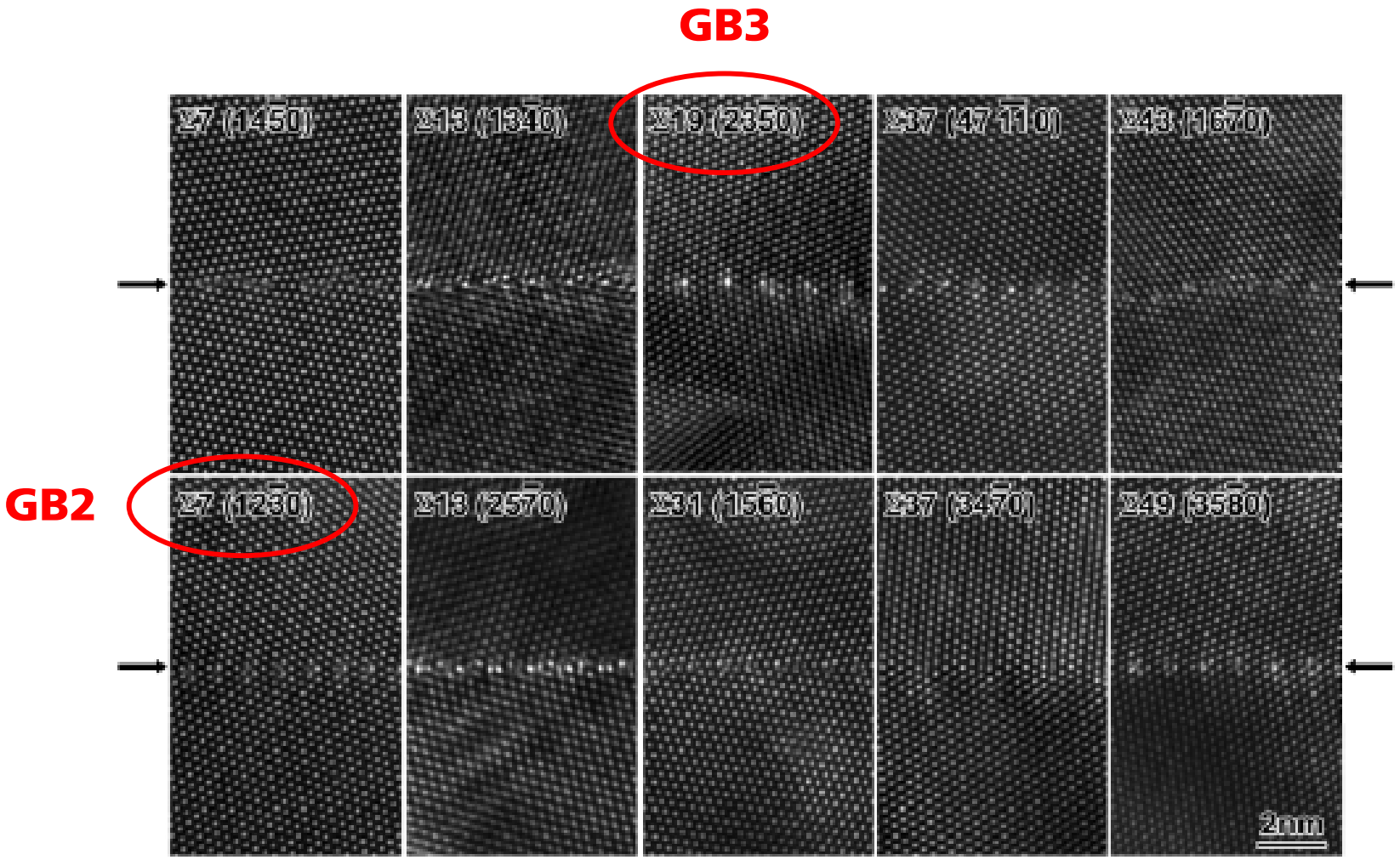
$$V_l^{SIC}(r) := V_l(r) - \alpha\big\langle \Psi_l^{pp}, V_{\mathrm{cor}}[n_l]\Psi_l^{pp}\big\rangle \Psi_l^{pp}(r)$$

- other SIC PP implementations, e.g.:

  Filippetti and Spaldin
  Phys. Rev. B 67 (2003) 125109
  Pemmaraju et al.
  Phys. Rev. B 75 (2007) 045101

bulk SIC: **Zn-3d** 100%, **O-2s** 100%, **O-2p** 80%, $\alpha = 0.8$

Grain boundaries in ceramic ZnO – bicrystal experiments



Sato et al., J. Am. Ceram. Soc. 90 (2007) 337-357

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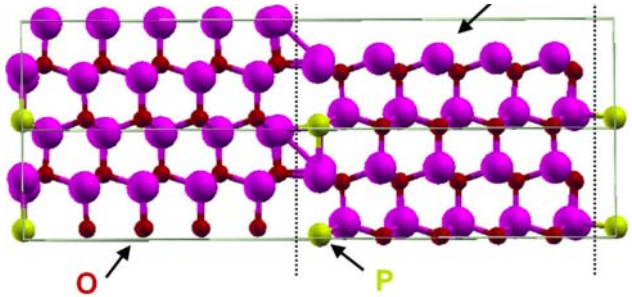
Supercells for three different GB in ZnO

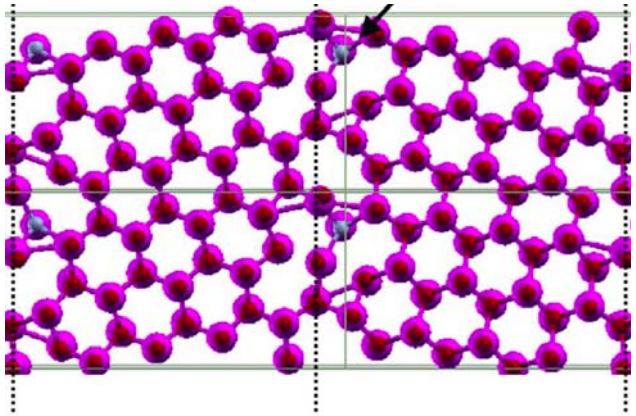
GB1:$(10\bar{1}0)[10\bar{1}0]$ $\Sigma 1$



80 atoms

E_{GB1} = 0.17 J/m^2

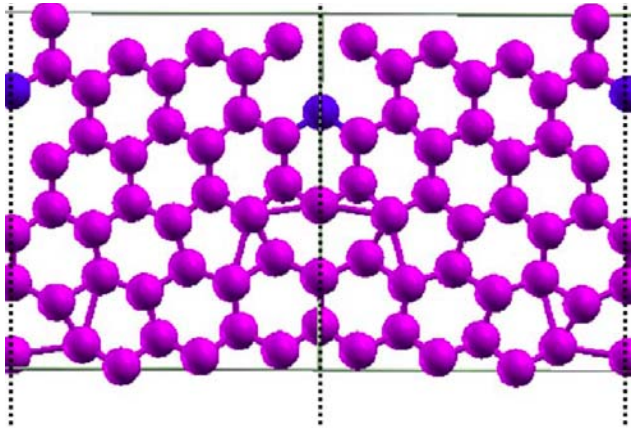
GB2:$(12\bar{3}0)[0001]$ $\Sigma 7$



112 atoms

E_{GB2} = 1.89 J/m^2

GB3:$(23\bar{5}0)[0001]$ $\Sigma 19$



152 atoms

E_{GB3} = 1.65 J/m^2

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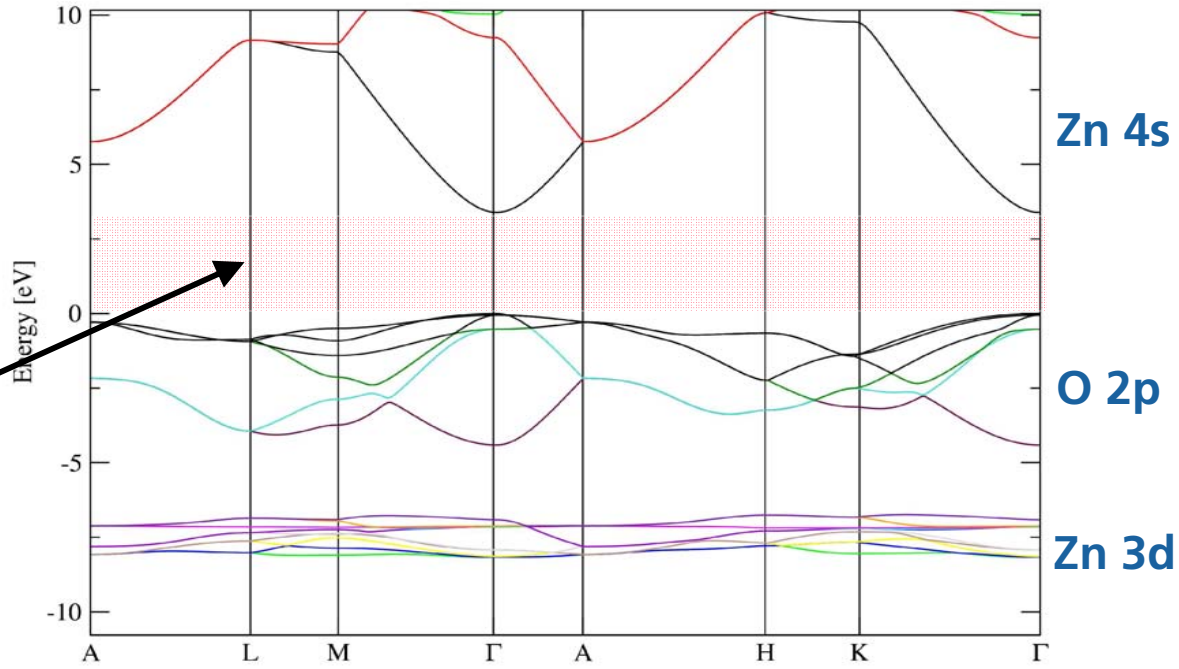
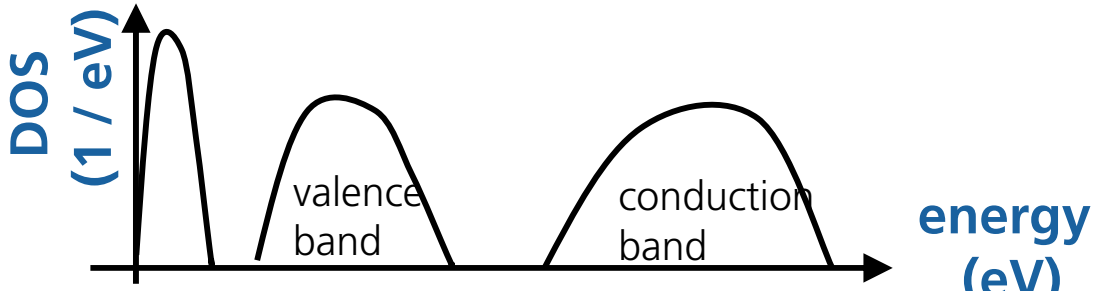
reference system: band structure of bulk ZnO

SIC-LDA

band gap 3.4 eV

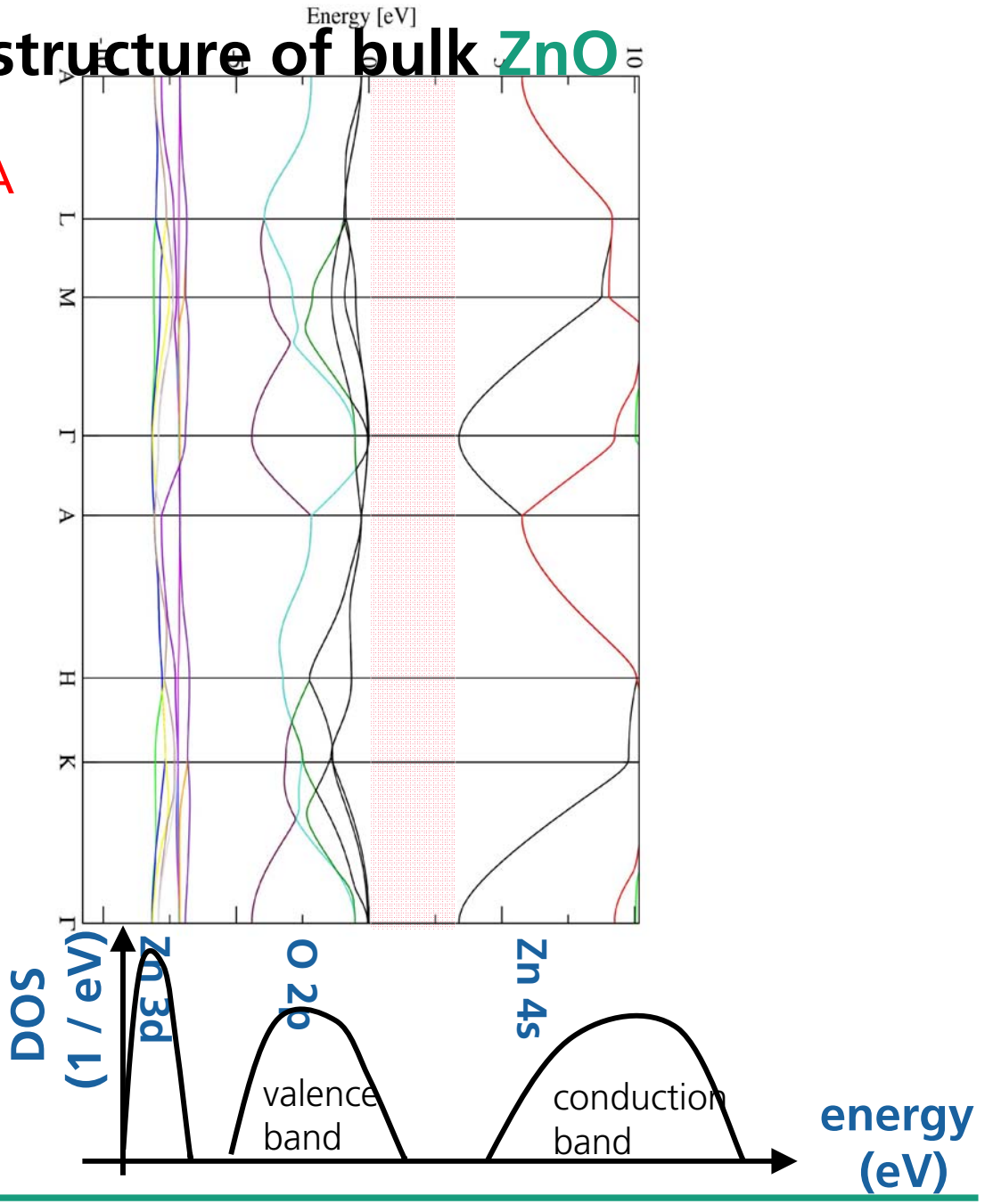




Fraunhofer IWM

reference system: band structure of bulk ZnO

SIC-LDA



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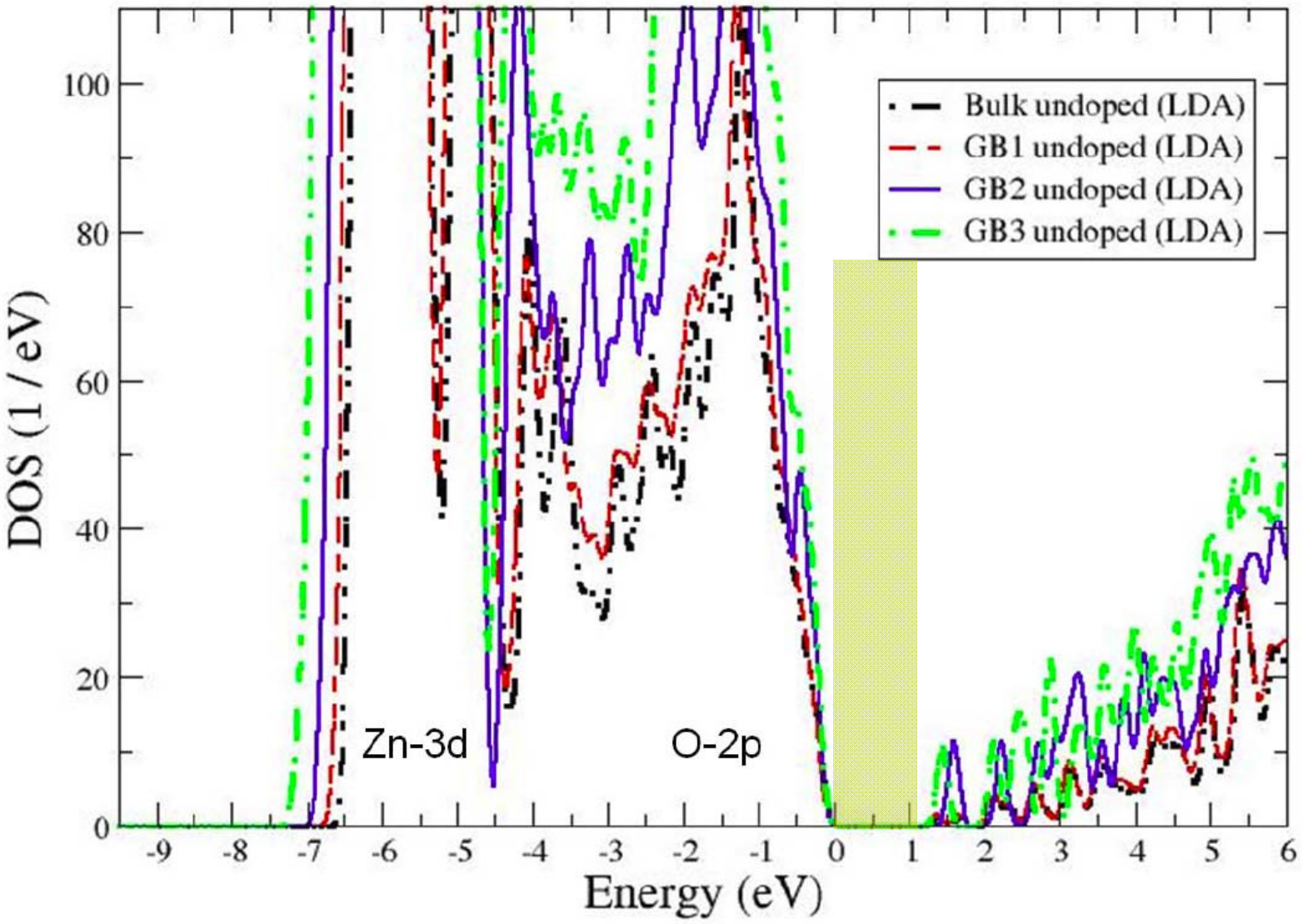
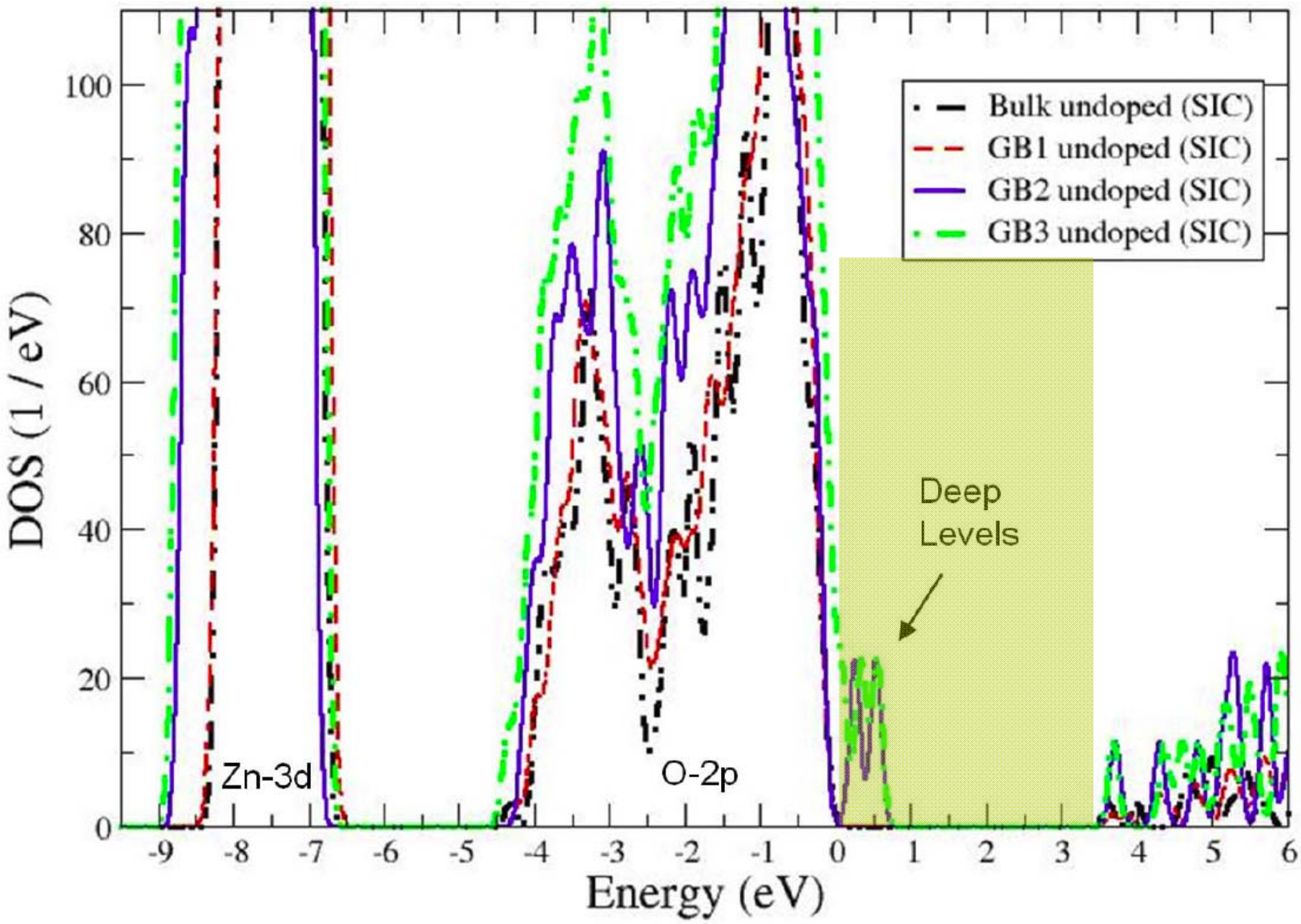
LDA: total DOS of undoped bulk and GB



Fraunhofer IWM

SIC: total DOS of undoped bulk and GB



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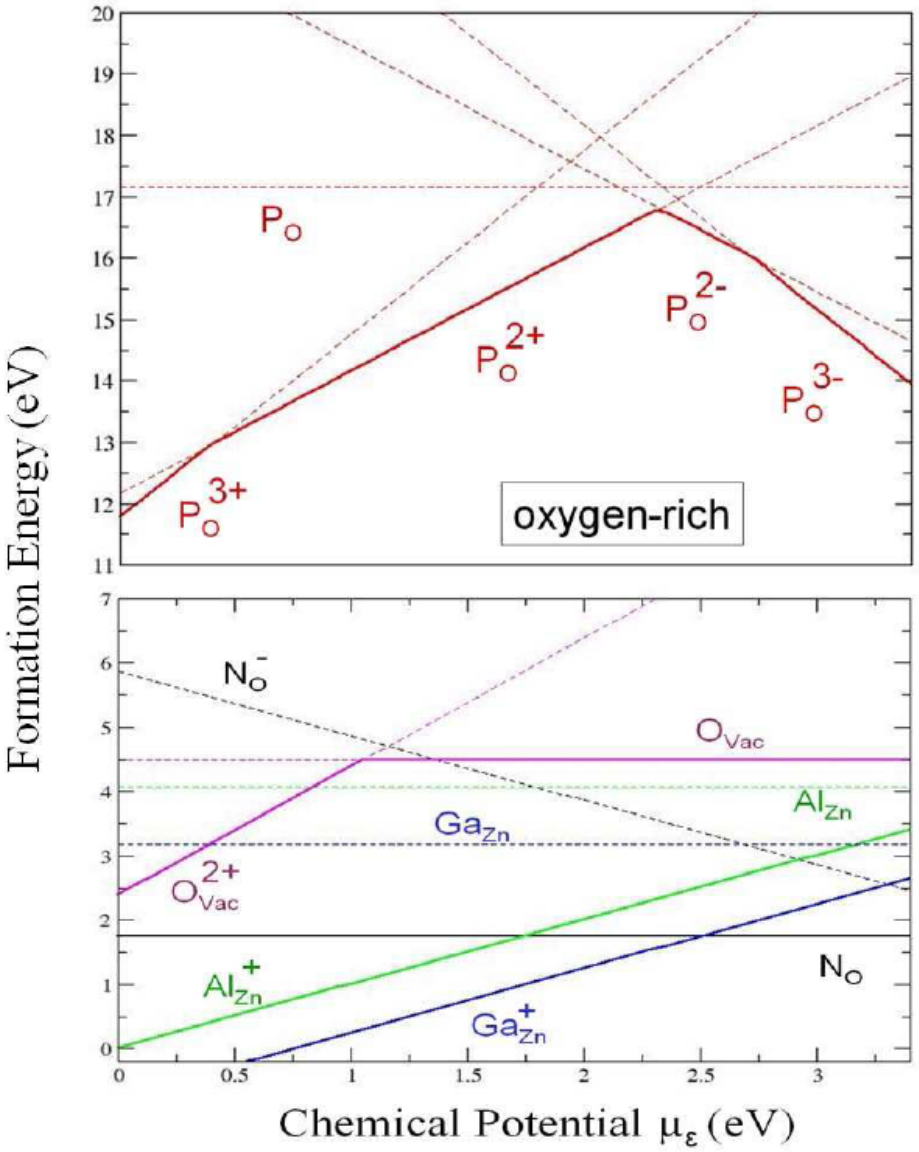
LDA + SIC: formation energies for dopants in bulk ZnO



- For calculation of defect formation energies see, e.g.:
  Van de Walle and Neugebauer
  J. Appl. Phys. 95 (2003) 3851

$$E_{\mathrm{f}}^{\mathrm{m}}(d,q) = E_{\mathrm{tot}}^{\mathrm{m}}(d,q) - E_{\mathrm{tot}}^{\mathrm{m}}(h,q=0) + \mu(h) - \mu(d) - q\,\mu_e$$

- For discussions of O vacancy in bulk ZnO see, e.g.:
  Lany and Zunger
  Phys. Rev. B 78 (2008) 235104
  Van de Walle
  J. Phys.: Condens. Matter 20 (2008) 064230
- (Zn vacancy in bulk ZnO is “tricky“ as well.)

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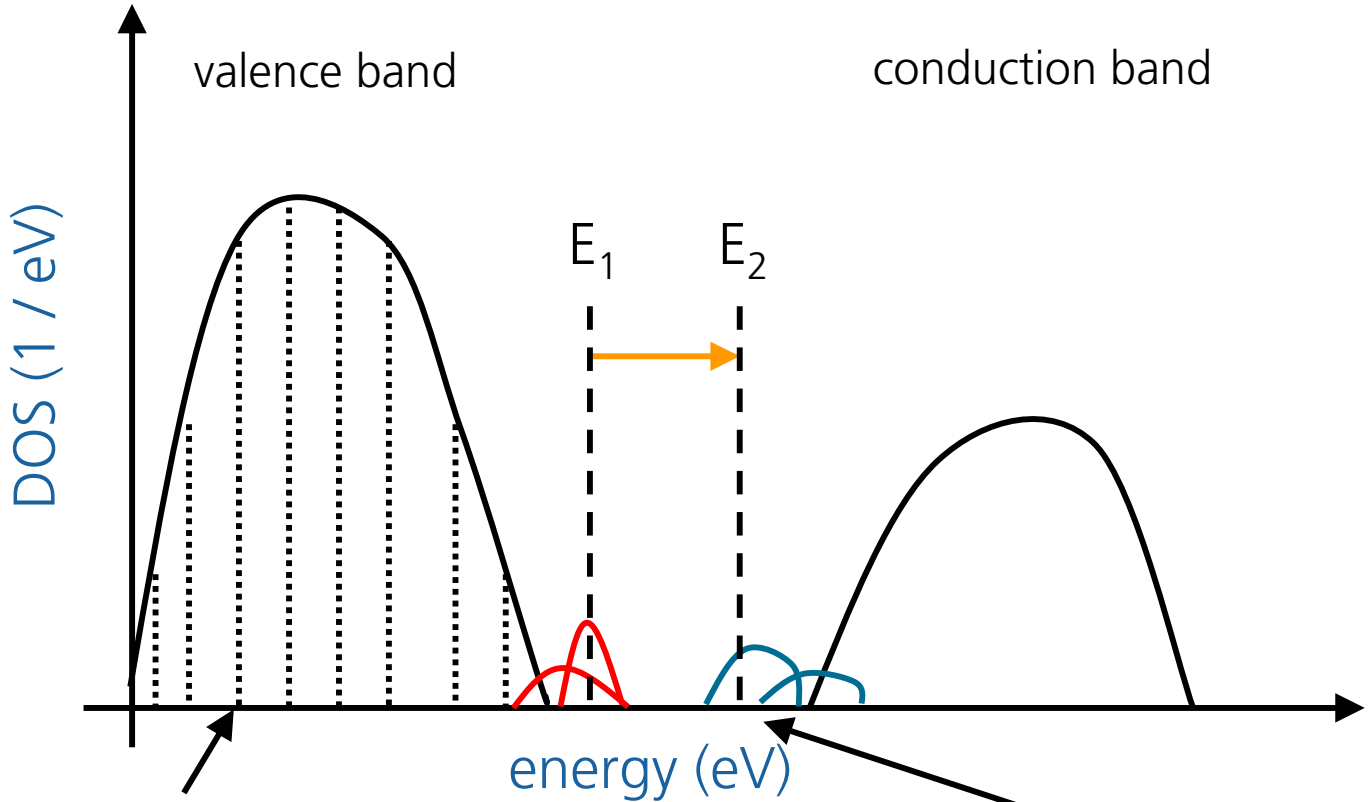
indicators for conductivity and transparency in band structure



1. undoped semiconductor
2. p-doping (bad)
3. p-doping (good)
4. n-doping (bad)
5. n-doping (good)

many states in the bulk band gap
⇨ **reduced transparency**
by transitions: **$hc / \lambda = E_2 - E_1$**

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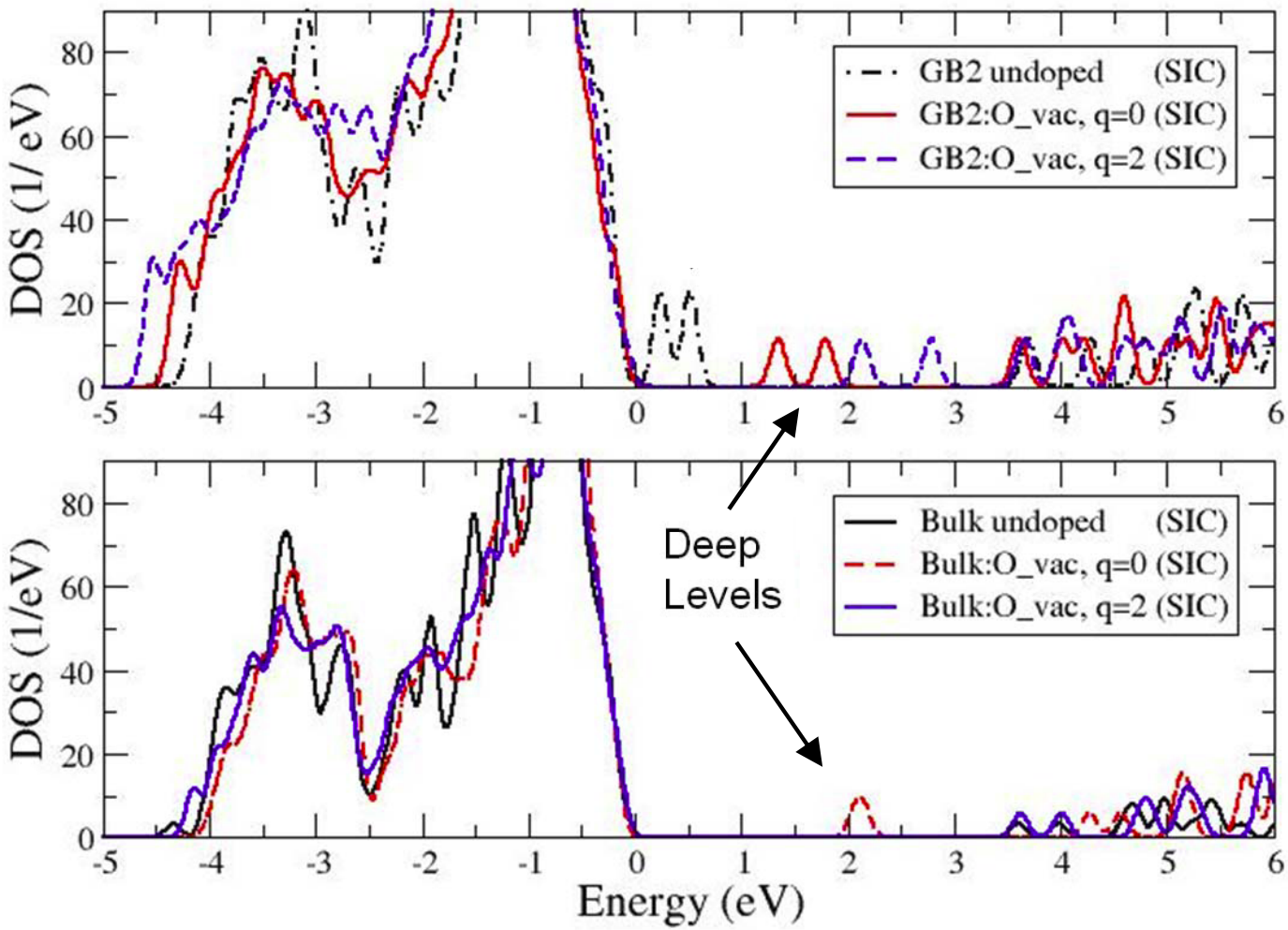
SIC: oxygen vacancy in ZnO



O_{vac} @ GB2:
bad conductivity,
and bad transparency

- exp.: „green luminescence"
  of ZnO with energy 2.4 eV

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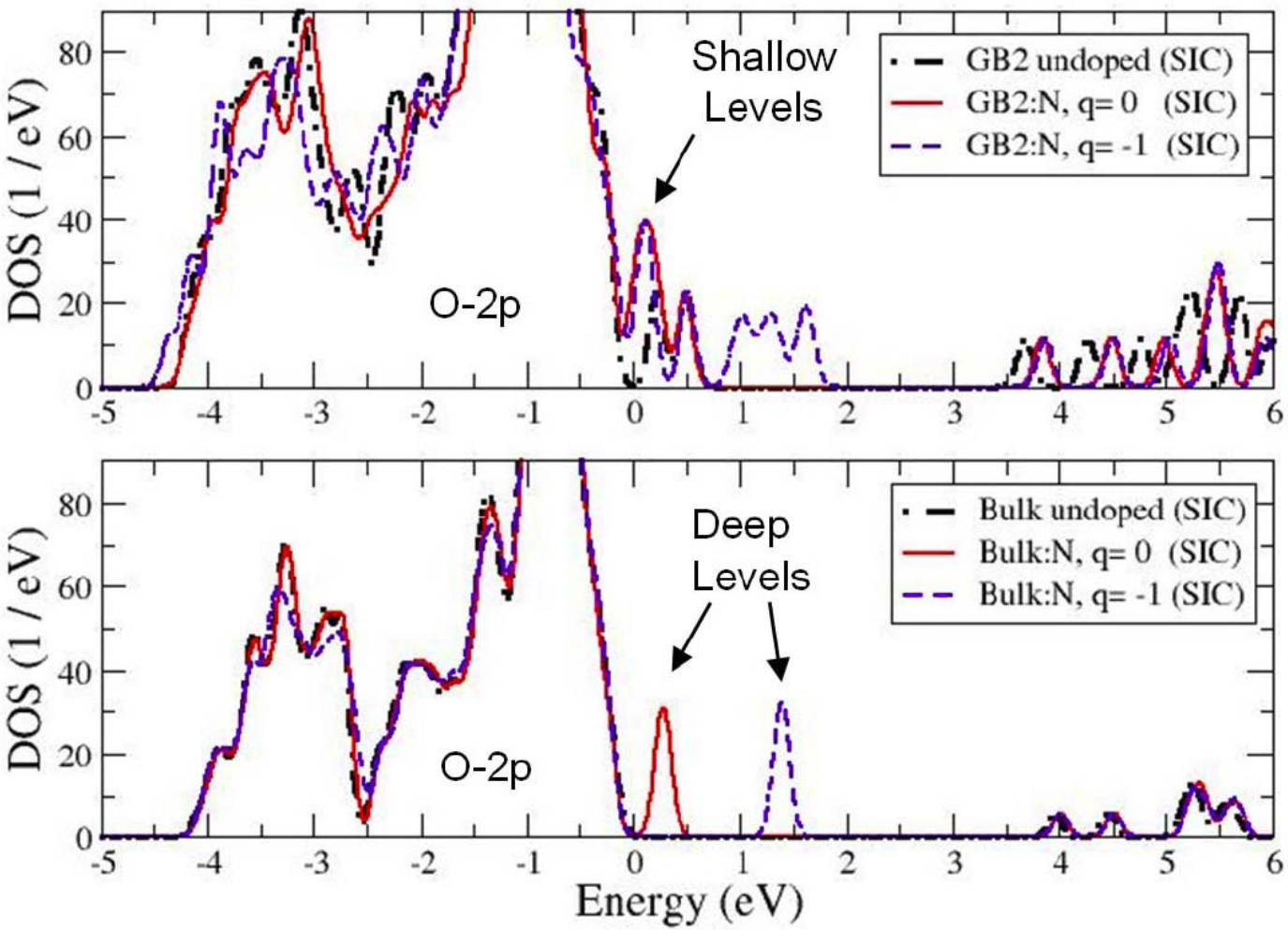
SIC: N_O dopant in ZnO



N_O @ GB2:
p-type conductivity at room temp. plausible, and good transparency

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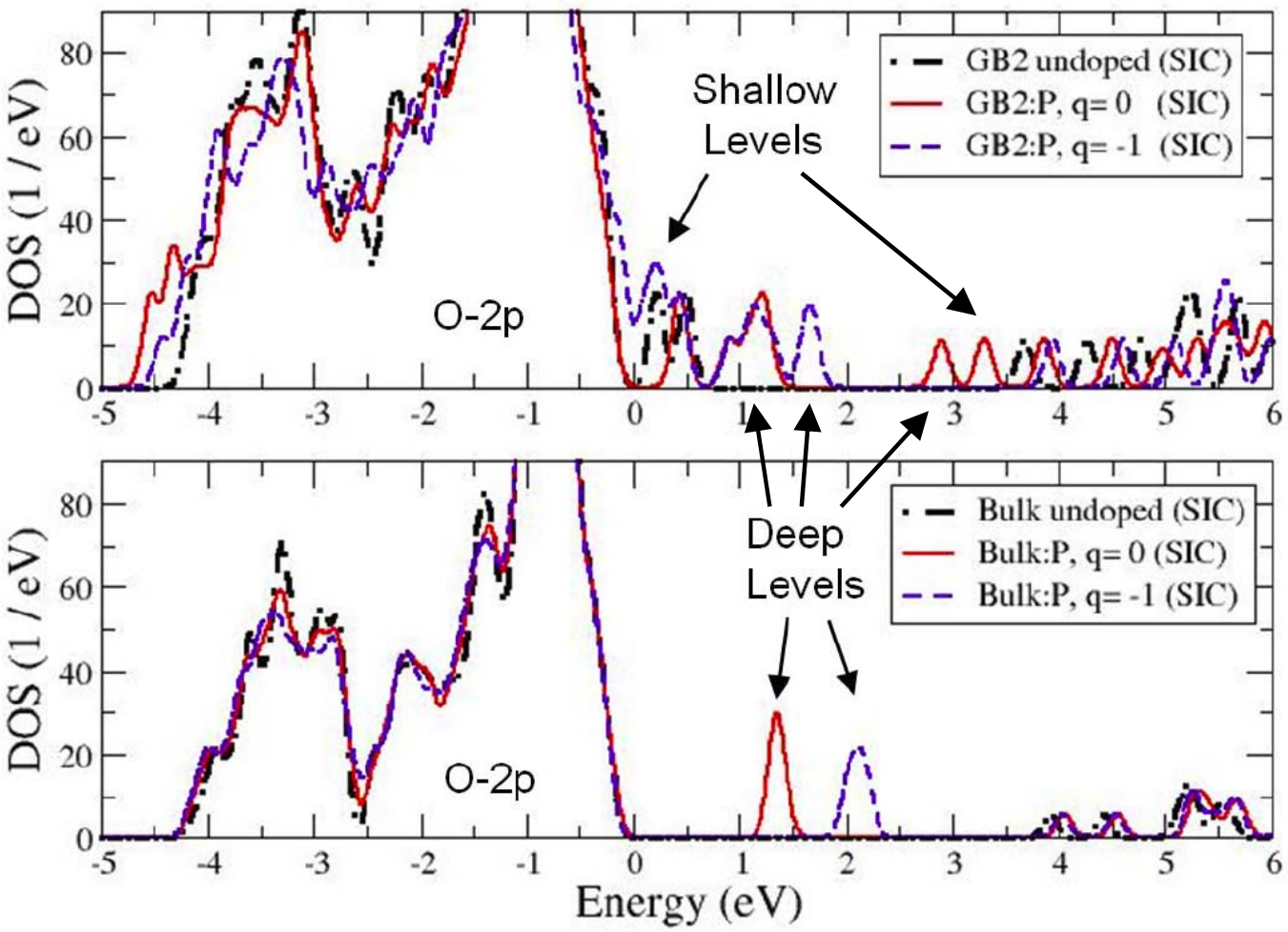
SIC: P_O dopant in ZnO



P_O @ GB2:
good conductivity,
but bad transparency

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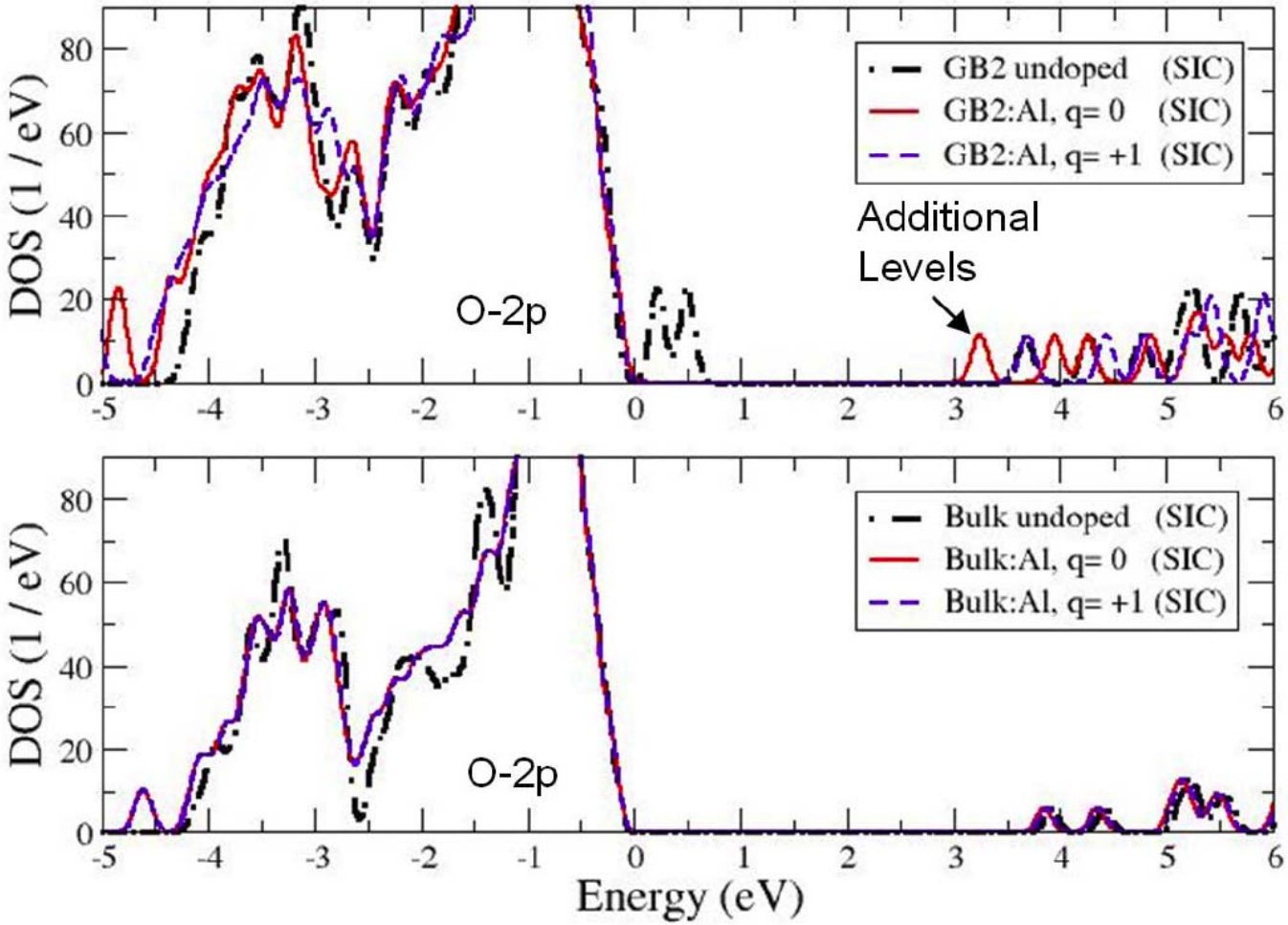
SIC: Al_{Zn} dopant in ZnO



Al_{Zn} @ GB2:
n-type conductivity at room temp. plausible, and good transparency

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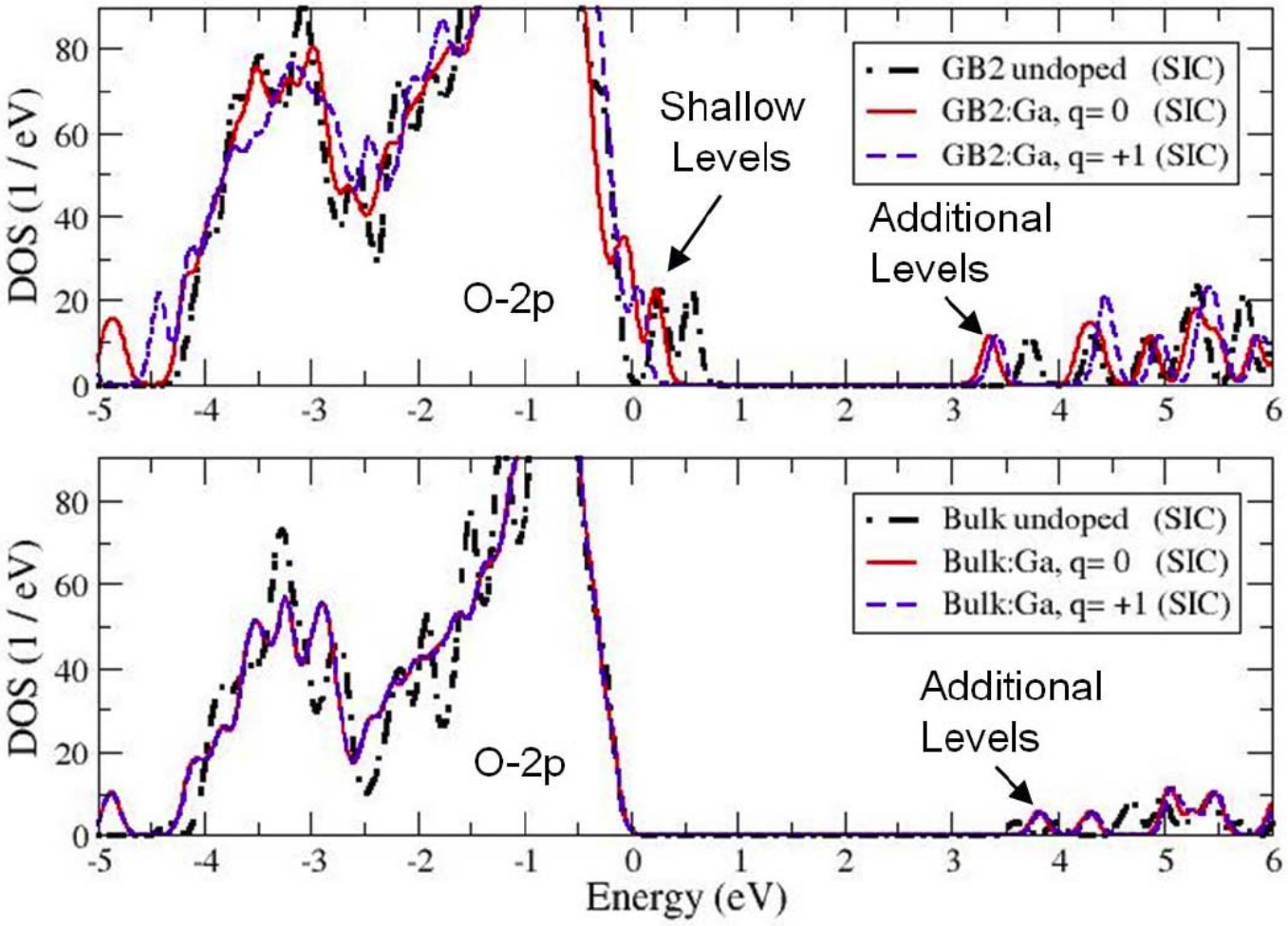
SIC: Ga_{Zn} dopant in ZnO



Ga_{Zn} @ GB2:
good conductivity,
and good transparency

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Conclusion I: ZnO

- **SIC:** self interaction correction via pseudopotentials
  - can describe band structure of ZnO better than LDA.
  - It is applicable to extended structural defects like grain boundaries.
- **grain boundaries** in polycrystalline ZnO
  - can cause deep defect levels in the band gap.
  - This SIC result is different from others' and our LDA results for GB!
- **dopants at grain boundaries** in ZnO
  - can cause shallow defect levels in the band gap.
  - Considering grain boundaries, not only perfect crystals, may help for better understanding of dopants in TCO ceramics?

Reference: W. Körner, C. Elsässer, Phys. Rev. B 81 (2010) 085324

Funding: Fraunhofer Society http://www.transparente-elektroden.de/

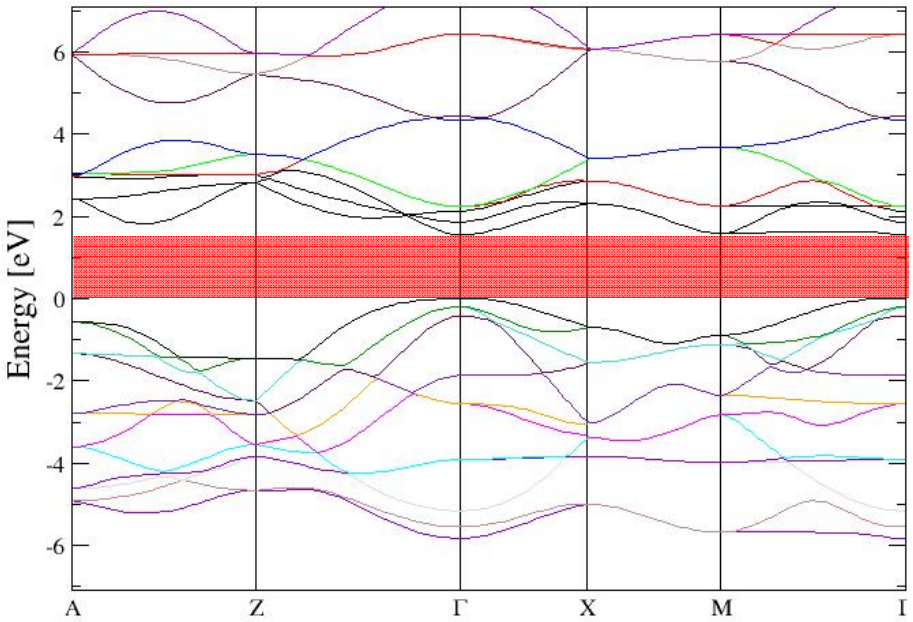
collection of supercell models for grain boundaries

material	boundary	interface	system size	γ [J/m^2]	
Wurtzite ZnO	$(10\bar{1}0)[10\bar{1}0]$ Σ1	$[10\bar{1}0]$ / 180°	80	0.17	**GB1**
	$(12\bar{3}0)[0001]$ Σ7	[0001] / 21.79°	56 / 112	1.81/1.88	**GB2**
	$(23\bar{5}0)[0001]$ Σ19	[0001] / 13.17°	152	1.65	**GB3**
Rutile TiO_2	(100)[100] Σ1	[100] / 180°	72	0.47	**GB1**
	(210)[001] Σ5	[001] / 36.87°	60 / 120	1.86/1.92	**GB2**
	(310)[001] Σ5	[001] / 53.13°	120	2.37	**GB3**
Anatase TiO_2	(100)[100] Σ1	[100] / 180°	72	0.64	**GB1**
	(021)[100] Σ5	[100] / 78.46°	120	0.89	**GB2**
	(031)[100] Σ5	[100] / 101.54°	120	2.36	**GB3**
	(120)[001] Σ5	[001] / 53.13°	120	2.10	**GB4**

TiO_2: band structure of Rutile

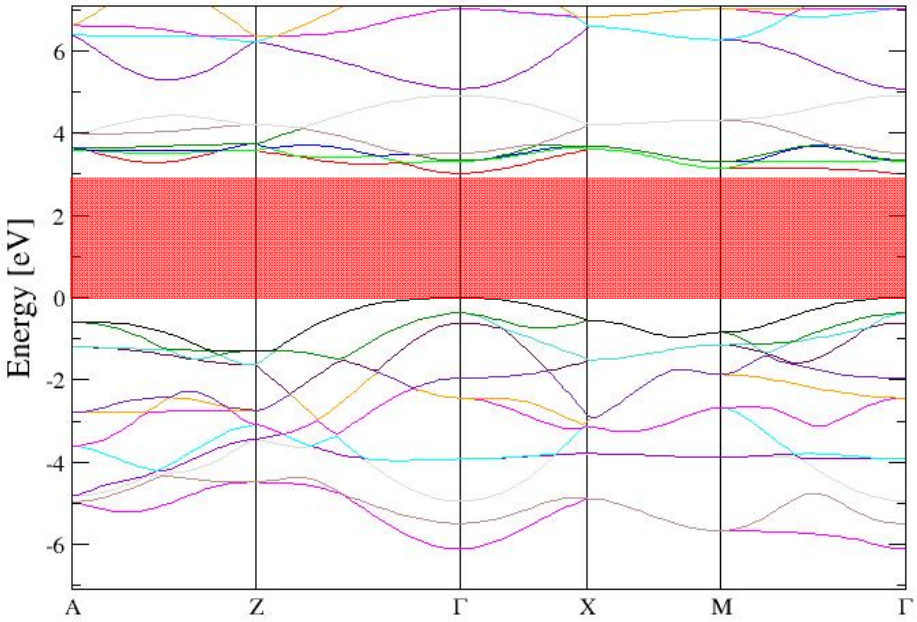
E_{gap} = 3.04 eV (exp.)

LDA



E_{gap} = 1.55 eV

SIC



Ti 3d

O 2p

E_{gap} = 3.02 eV

bulk SIC: **Ti** (LDA), **O-2s** 100%, **O-2p** 90%, $\alpha = 0.8$

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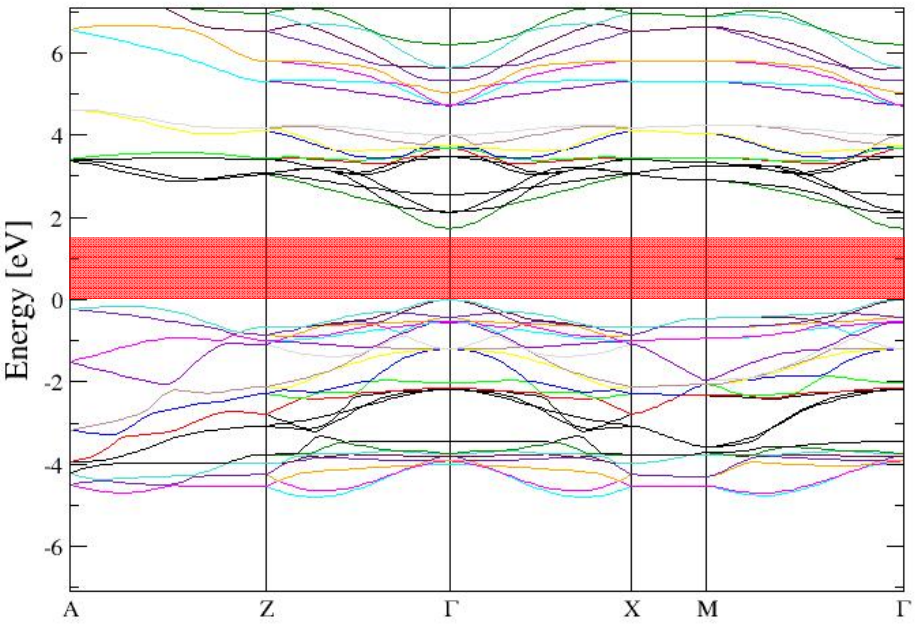
TiO2: band structure of Anatase

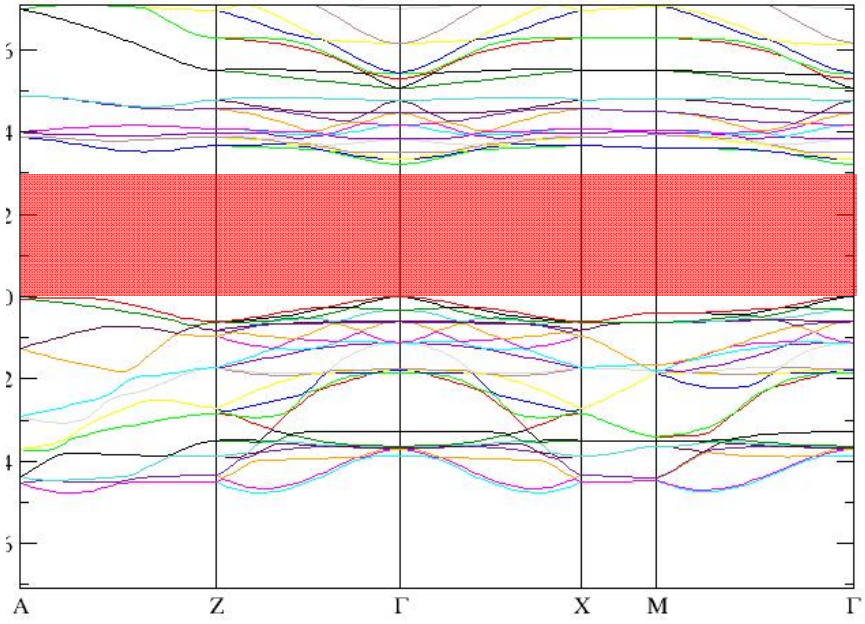
E_{gap} = 3.20 eV (exp.)

LDA



E_{gap} = 1.73 eV

SIC



Ti 3d

O 2p

E_{gap} = 3.22 eV

bulk SIC: **Ti** (LDA), **O-2s** 100%, **O-2p** 80%, $\alpha = 0.8$

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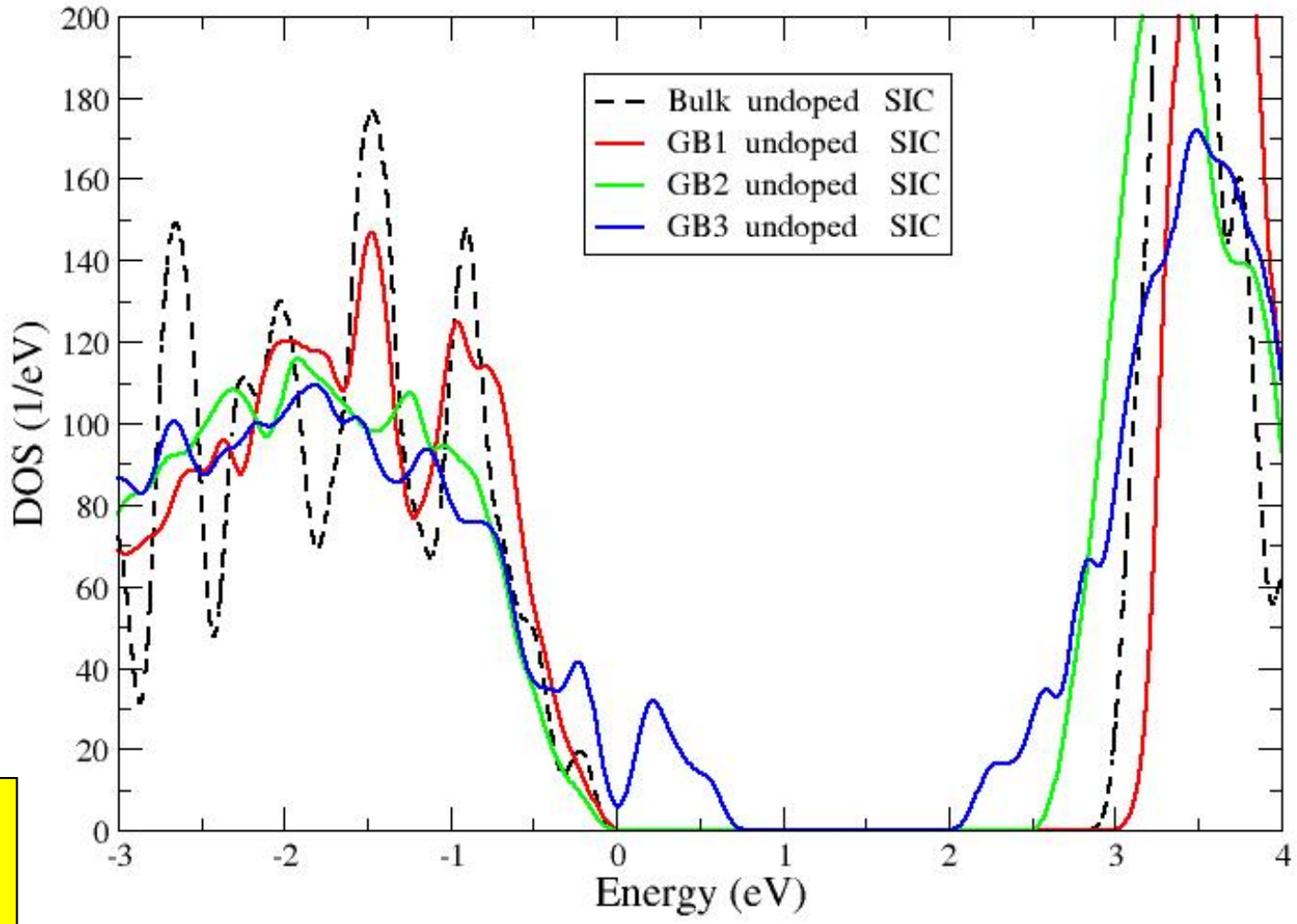
DOS of undoped GB in TiO_2 (rutile)

SIC-LDA

- „deep levels“ for GB3
- GB1 is structually very similar to bulk



O atoms at GB3 have only two Ti atoms as nearest neighbours.

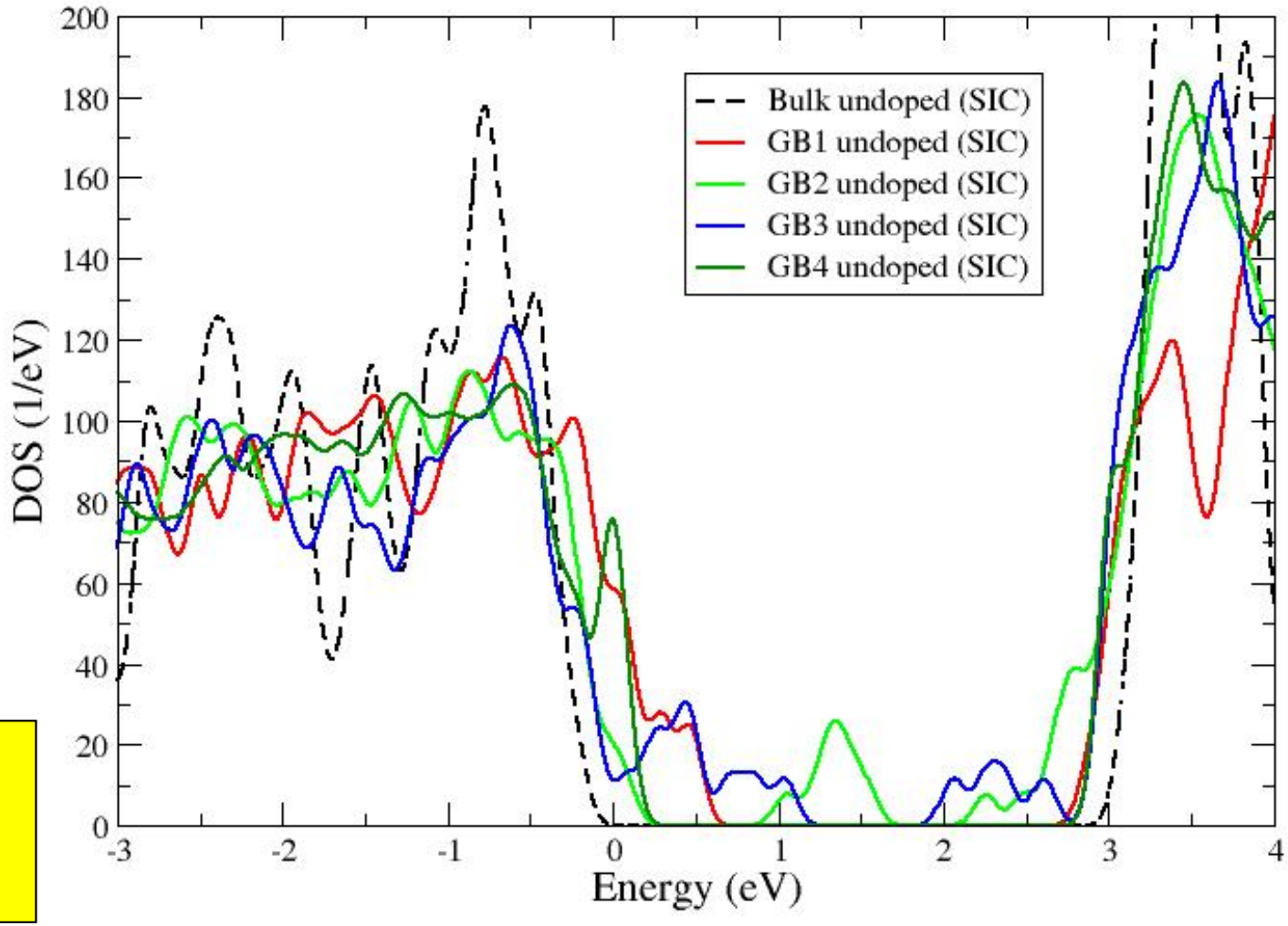
Fraunhofer IWM

DOS of undoped GB in TiO_2 (anatase)

- „deep levels“

  for GB1,GB2 and GB3

SIC-LDA



O atoms at GB1, GB2, and GB3 have only two Ti atoms as nearest neighbours.

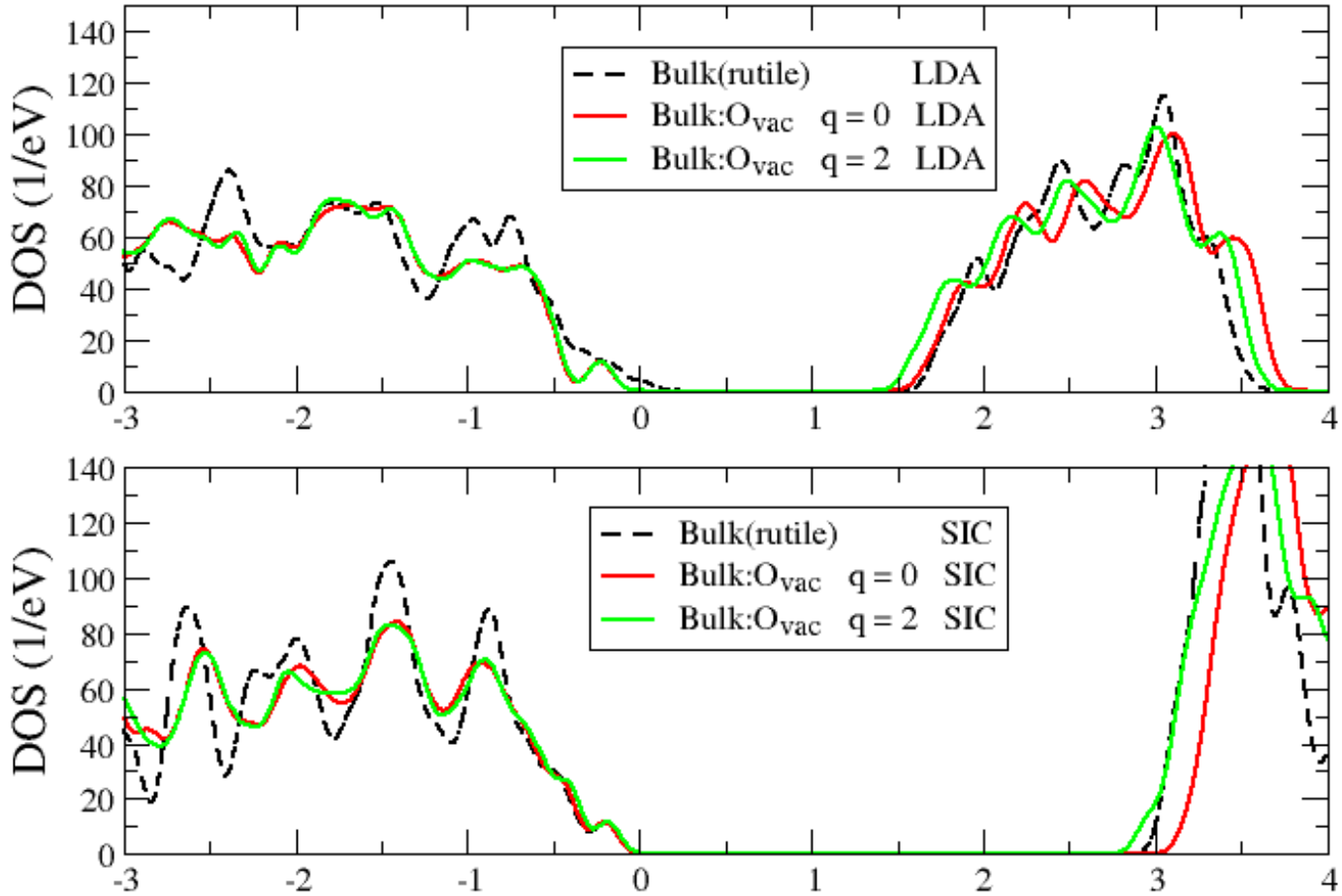
Fraunhofer IWM

O vacancy in TiO_2 (rutile)

- no donor levels

  (in accordance with other DFT studies)

comparison LDA vs SIC



Fraunhofer IWM

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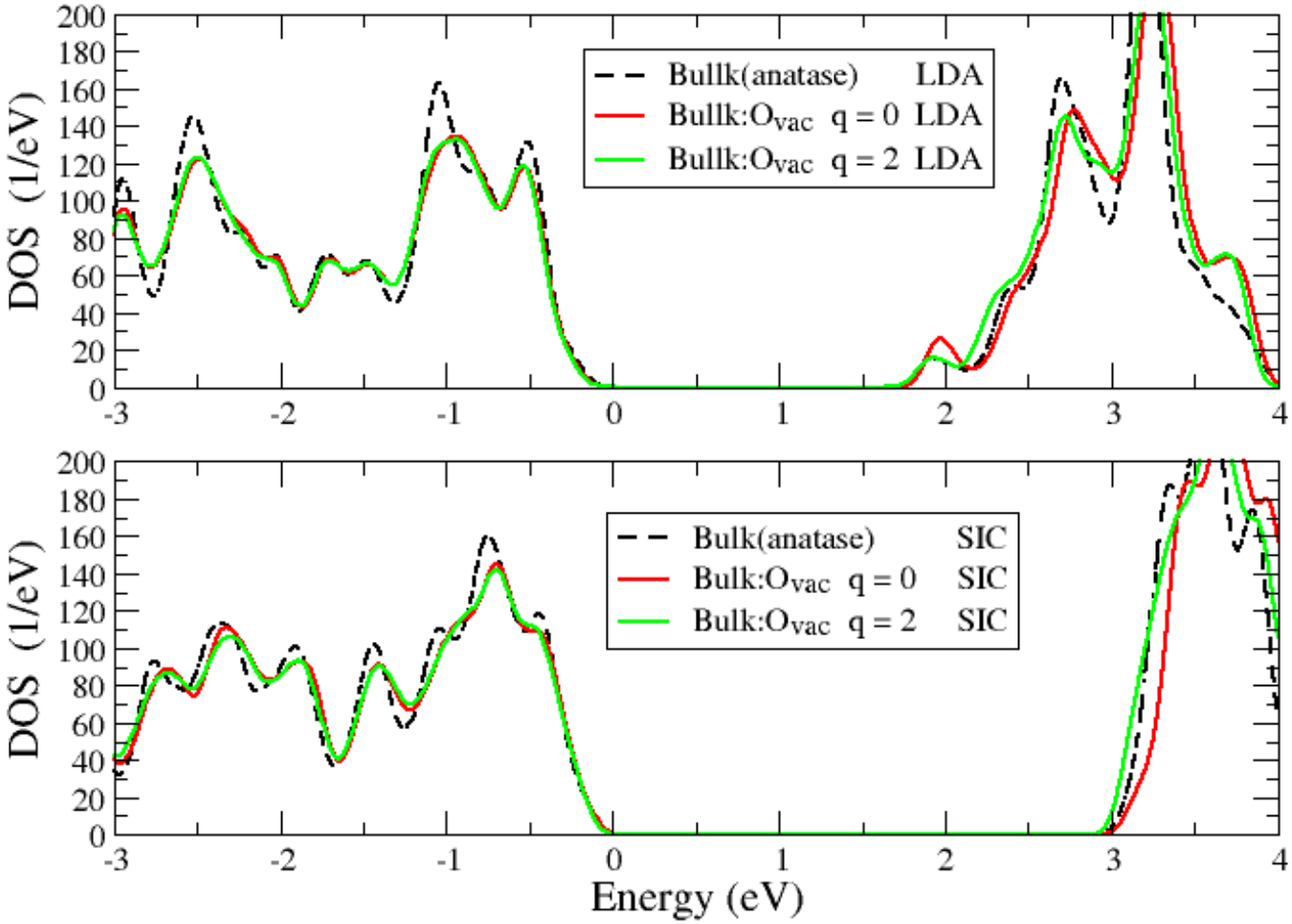

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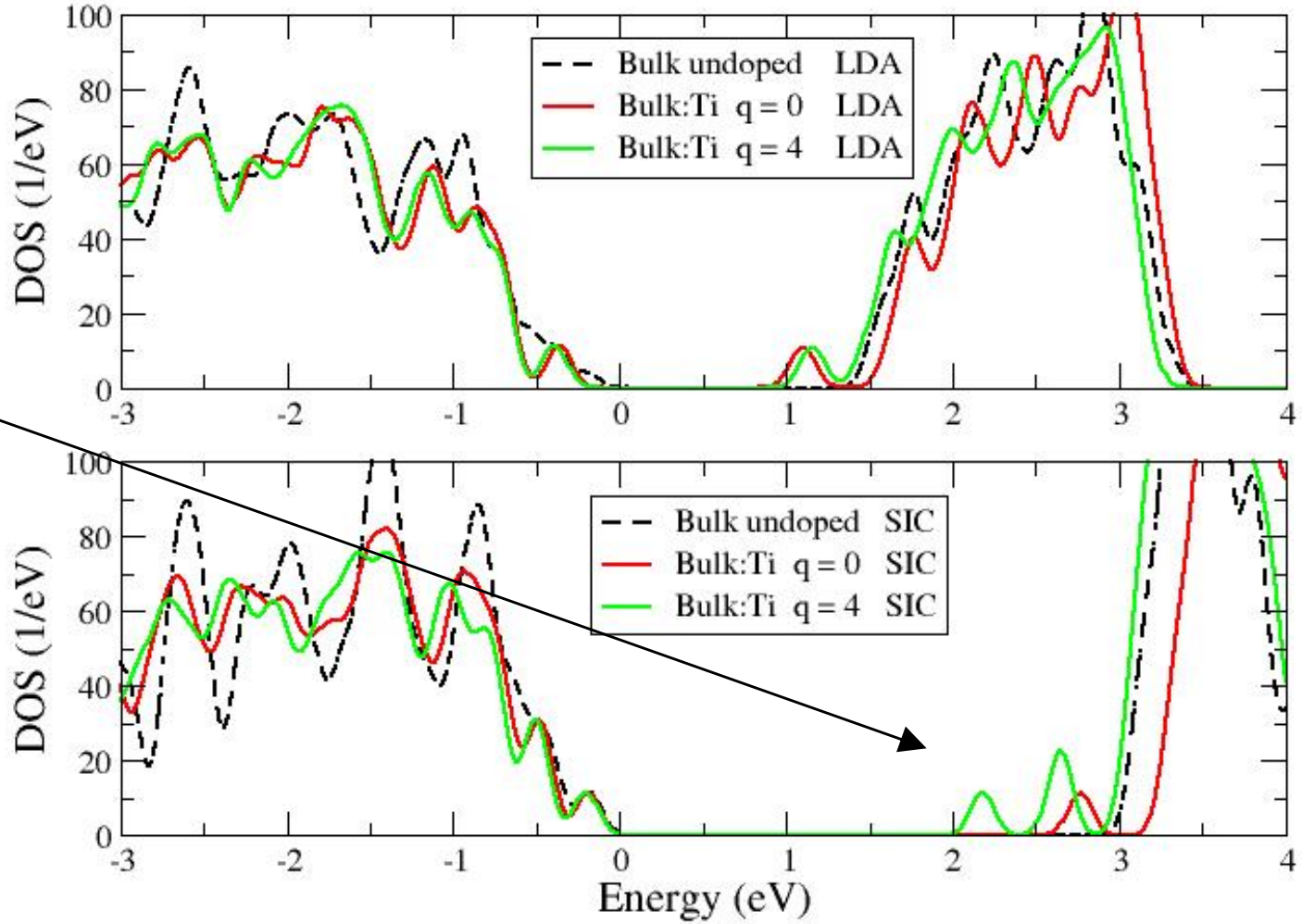
Interstitial Ti atom in TiO_2 (rutile)

comparison LDA vs SIC

- donor levels



- exp.: "blue coloration" of reduced TiO_2 (rutile) with energy 0.75eV

Cronemeyer et al. Phys. Rev. **82**, 975 (1951)

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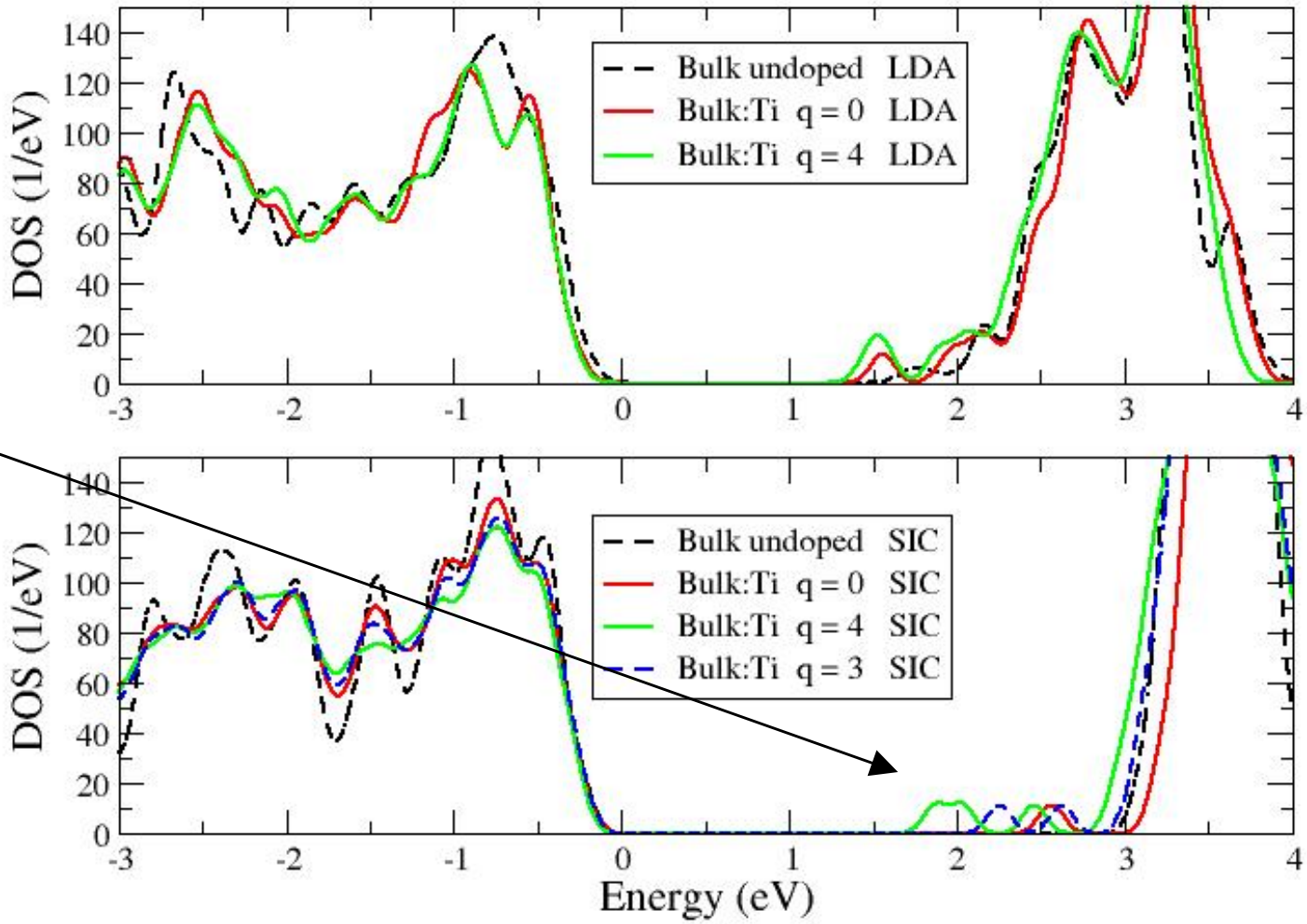
Interstitial Ti atom in TiO_2 (anatase)

comparison LDA vs SIC

- donor levels



Hence:
1. Anatase und Rutile show very similar behaviour.
2. Already LDA yields donor states.
3. SIC yields levels which could explain „blue coloration“.

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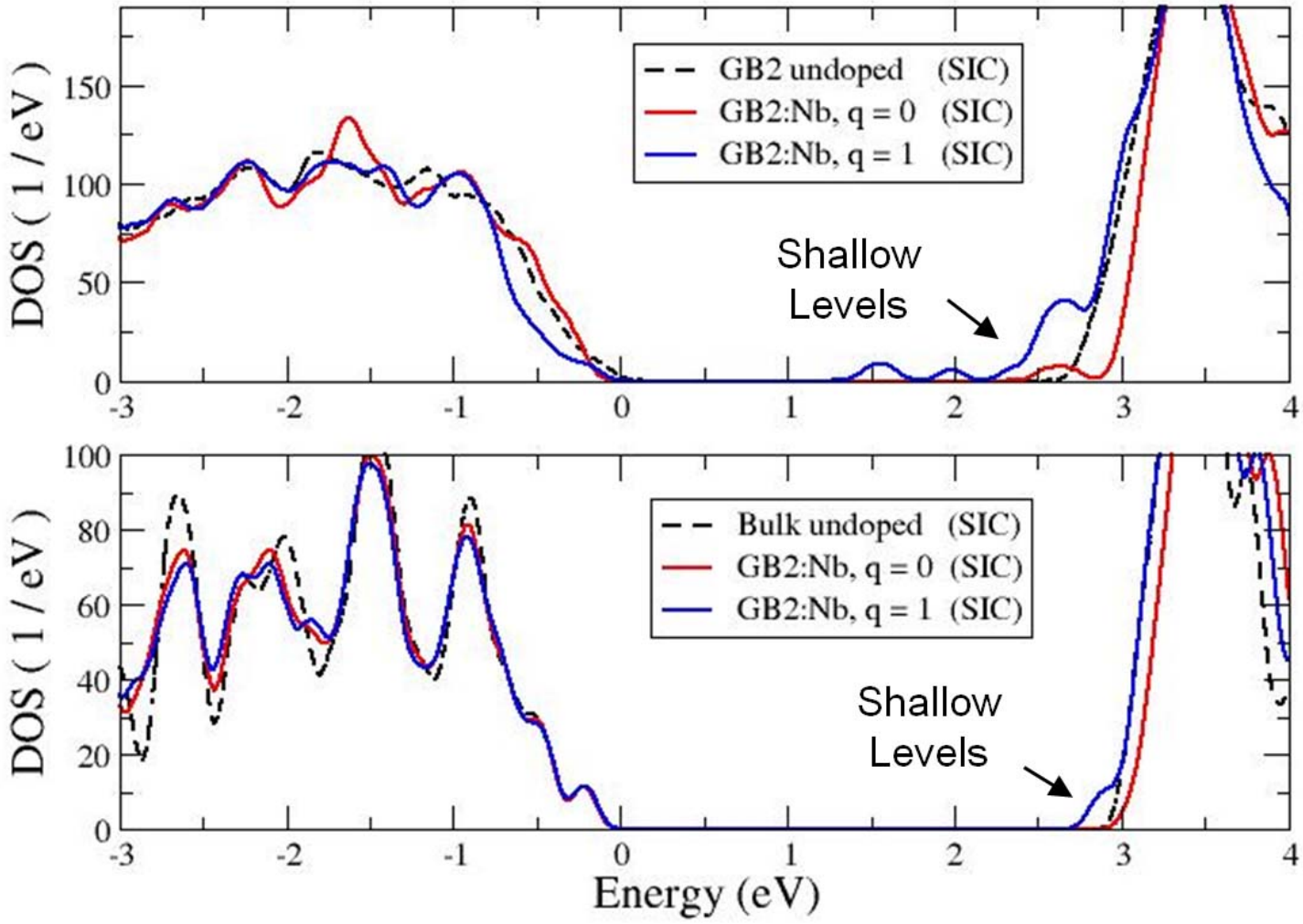
TiO_2 (rutile) doped with Nb_{Ti}

- Nb causes additional levels below the conduction-band edge.

→ hence: Nb is suitable for n-doping.

comparison bulk vs GB2



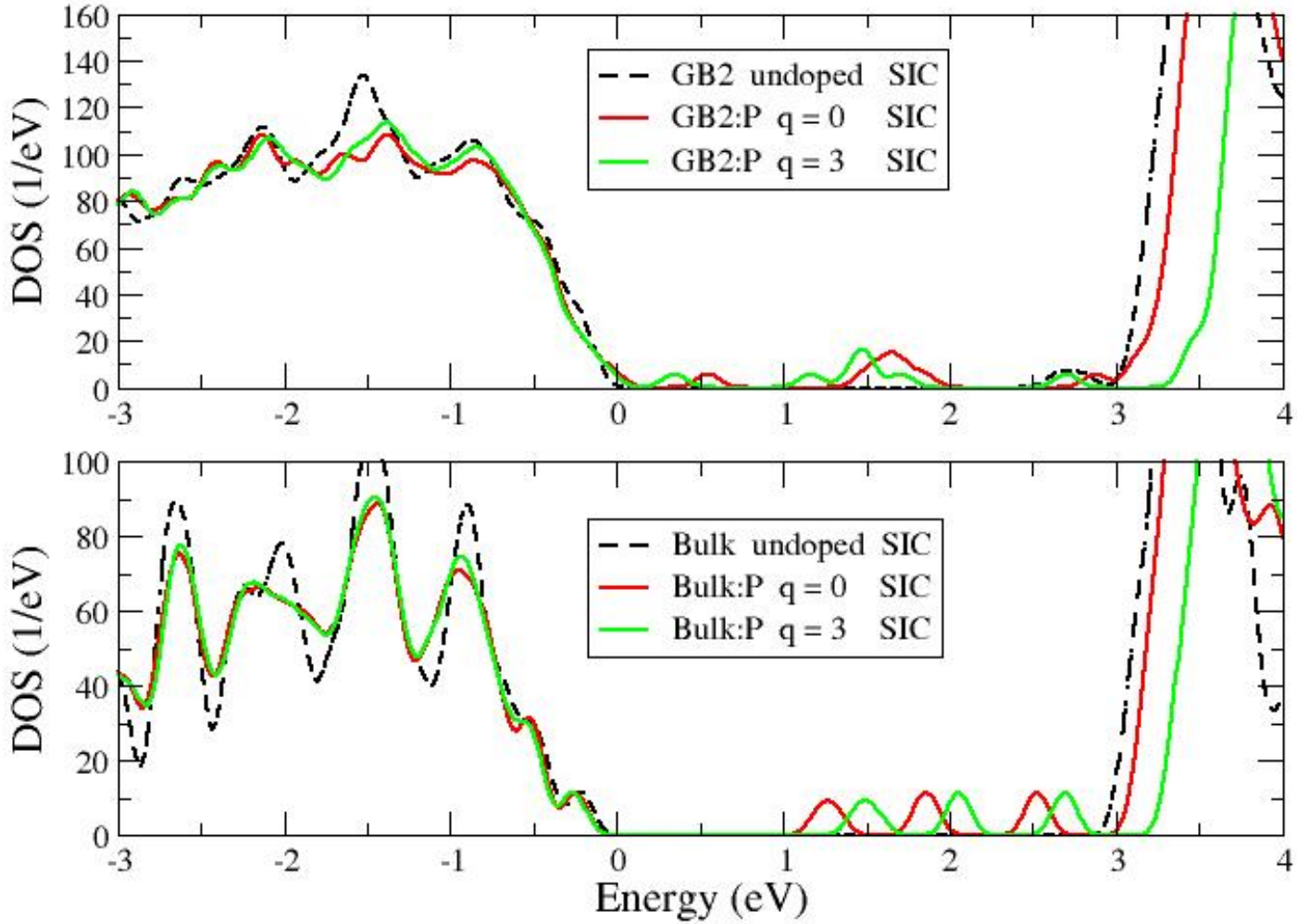
Fraunhofer IWM

TiO_2 (rutile) doped with P_O

Vergleich Bulk vs GB2

- At GB2 the additional levels are more smeared out than in bulk.

→ nevertheless: P is not suitable for p-doping.



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Conclusion II: ZnO and TiO_2

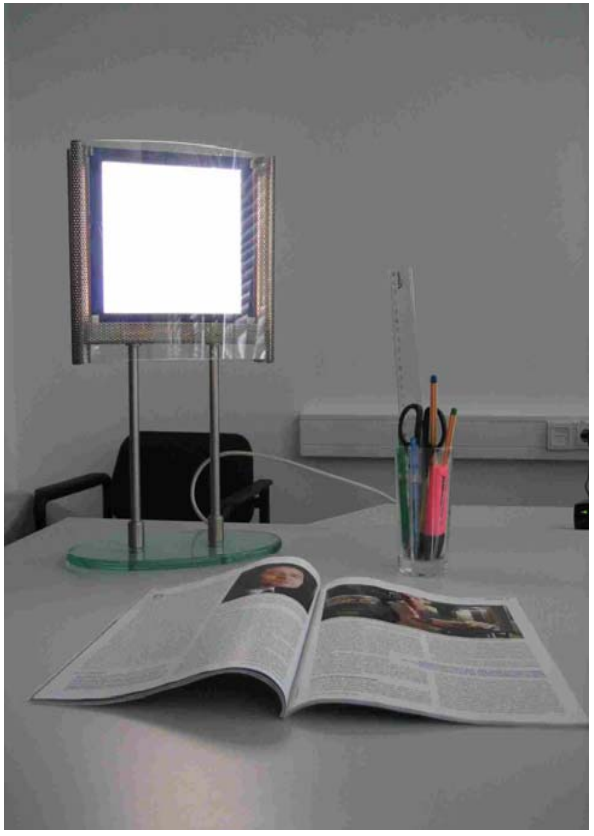
- Undoped grain boundaries of ZnO and TiO_2, which have O atoms with "dangling bonds", show "deep levels".
- TiO_2: Anatase and Rutile show only little differences.
- Intrinsic point defects
  - O-vacancy in ZnO and Ti-interstitals in TiO_2 may be related to n-conductivity.
  - experimental „green luminescence" (2.4eV) of ZnO or "blue coloration" (0.75eV) of TiO_2 may be understood from theoretical SIC results.
- Extrinsic point defects

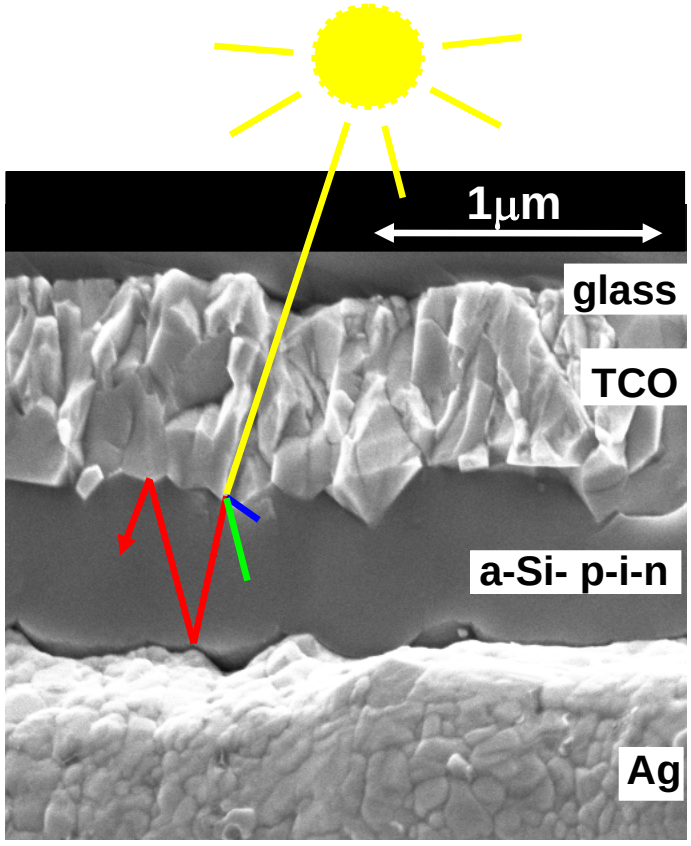
  N is a good candidate for p-doping in both ZnO and TiO_2

  Al and Ga are good candidates for n-doping in ZnO, Nb is the best found one in TiO_2.

First-principles DFT study of dopant elements at grain boundaries in the TCO materials ZnO and TiO_2

Wolfgang Körner and Christian Elsässer, Fraunhofer IWM





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Physical modelling of materials
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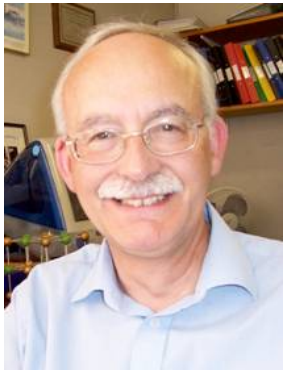

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