Theory of Hydrogen-Related Levels in Semiconductors and Oxides

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Acknowledgments

- **Computations**

  J. Neugebauer (Max-Planck-Institut, Düsseldorf)

  A. Janotti (UCSB)

  S. Limpijumnong (Suranaree U. Tech., Thailand)

  B. Tuttle (Penn State University)

- **Support**

  AFOSR; ONR

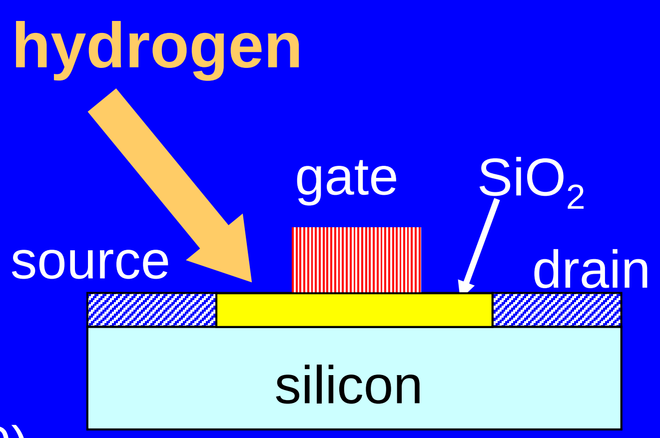
  Palo Alto Research Center

  Alexander von Humboldt Foundation

  Fritz-Haber-Institut & Paul-Drude-Institut, Berlin

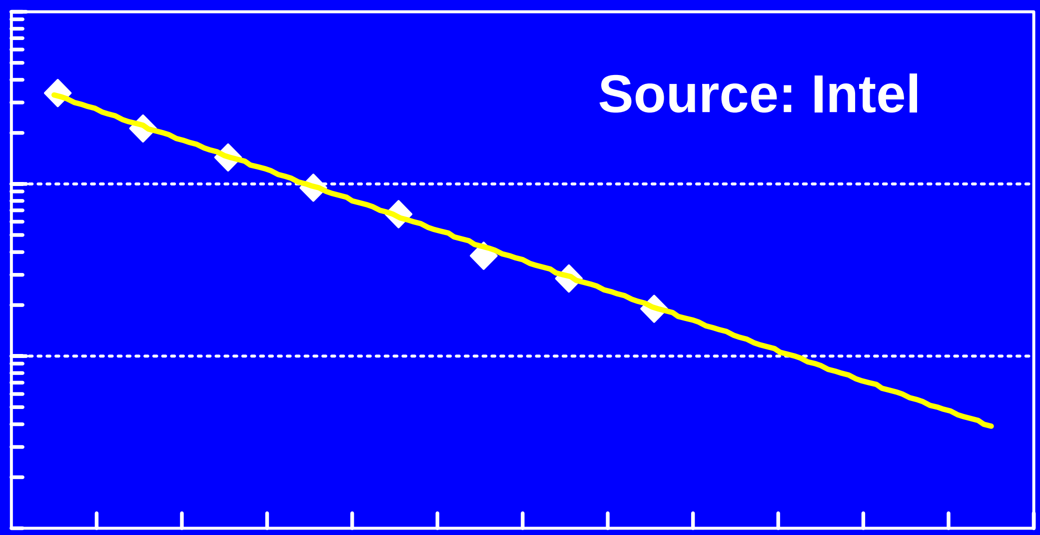
Motivation for studying hydrogen

- Omnipresent impurity
  - Growth
    - vapor-phase transport, hydrothermal growth, MOCVD, MBE, sputtering (H_2 atmosphere), …
  - Processing: forming gas anneal, …
- Beneficial effects & applications
  - Passivation of defects
    - Si/SiO_2
    - Reliability? (deuterium)
    - High-k dielectrics?
  - C. G. Van de Walle and B. Tuttle, IEEE Trans. Electr. Dev. **47**, 1779 (2000).



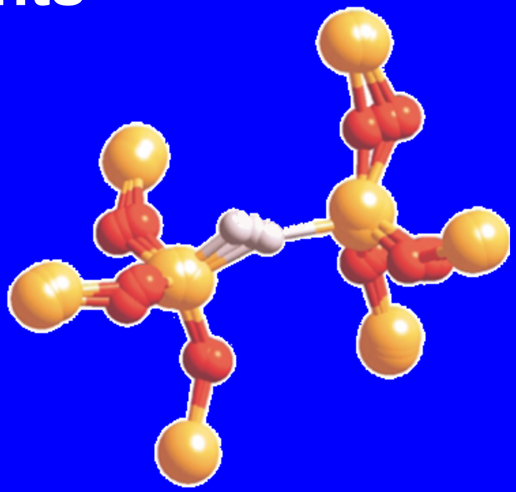
Motivation for studying hydrogen

- Unintended / detrimental effects
  - Passivation of dopant impurities
    - DRAM variable retention time
    - Nanoscale MOSFETs



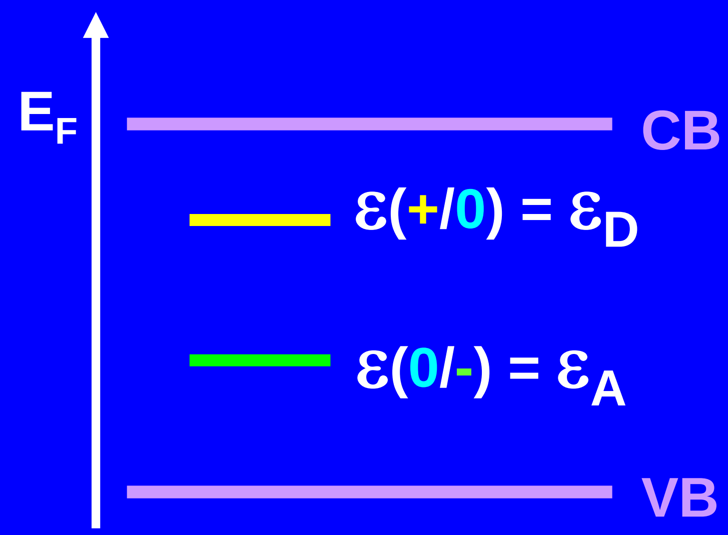
Motivation for studying hydrogen

- **Unintended / detrimental effects**
  - **Passivation of dopant impurities**
    - **DRAM variable retention time**
    - **Nanoscale MOSFETs**
  - **Trapping of hydrogen in oxide**
    - **Stress-induced leakage currents**
      - Blöchl and Stathis, Phys. Rev. Lett. **83**, 372 (1999).
    - **Charging of interface**
      - Afanas'ev and Stesmans, Appl. Phys. Lett. **72**, 79 (1998).

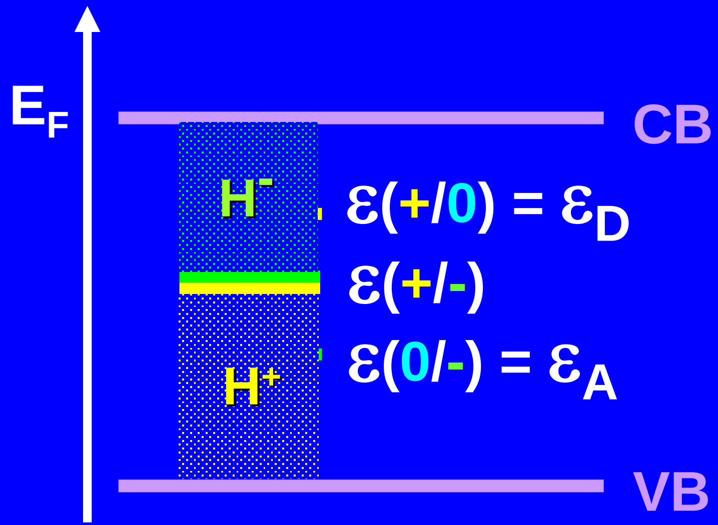


Hydrogen impurities

- Understanding “interstitial” hydrogen
  $\Rightarrow$ interactions with defects and impurities
- Hydrogen is **electrically active!**
  - H^0: rarely important
  - $H^+ \rightarrow$ donor
  - $H^- \rightarrow$ acceptor
- Amphoteric impurity
  - relative stability of H^+/H^- depends on Fermi level



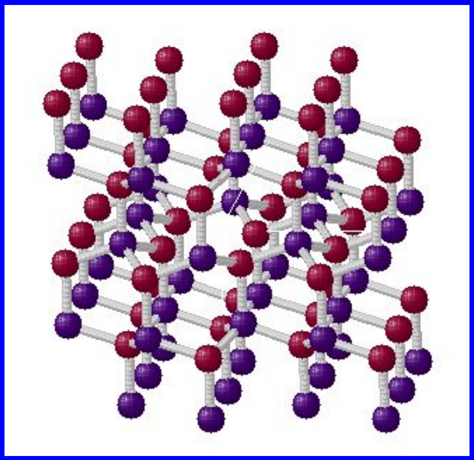
Example: interstitial H in GaN



Amphoteric impurity:

- **H^+ in *p*-type / H^- in n-type**

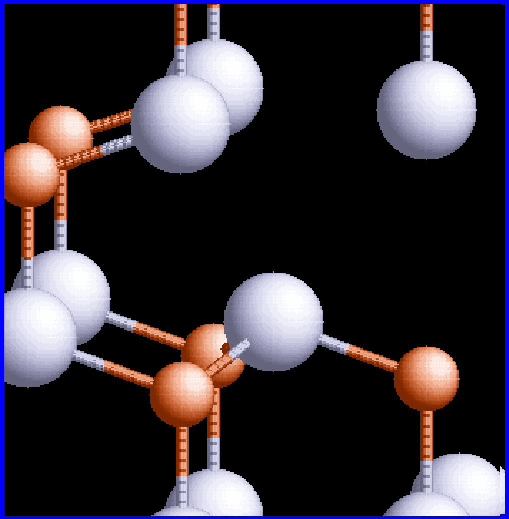
➔ Always counteracts prevailing conductivity



- **First-principles calculations**
  - Density-functional theory
  - Pseudopotentials / Atomic relaxations
- **Applies to: Si, …; GaAs, AlAs, GaN, AlN, …; ZnSe, …**
- **What about ZnO?…**

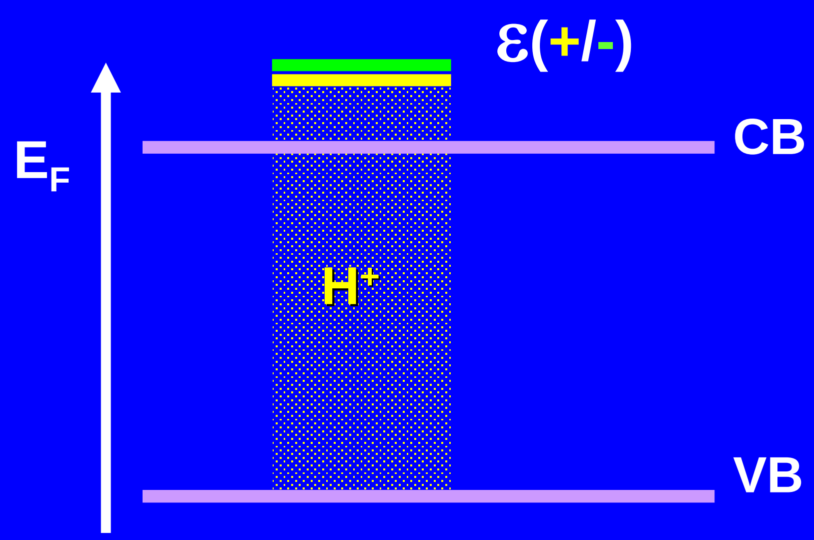
Zinc oxide devices

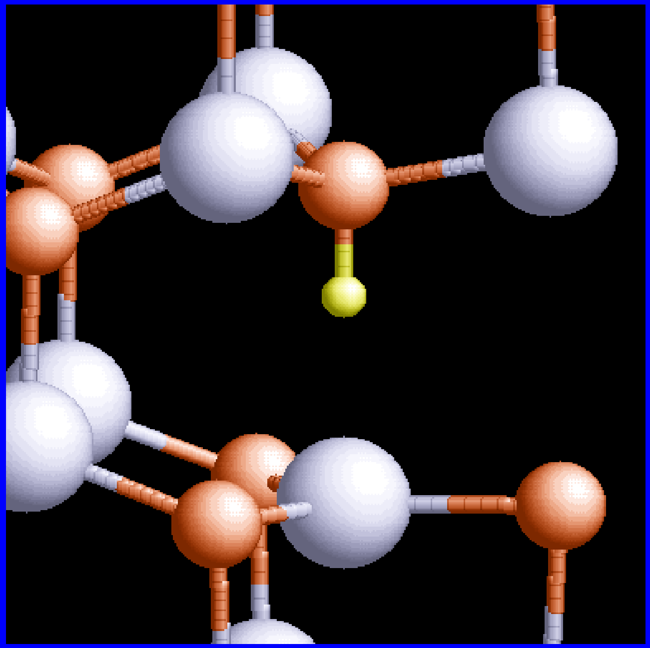
- **Applications in optoelectronics**
- **Zinc oxide: typically *n*-type**
  - **Conductivity due to electrons**
  - **Cause: heavily debated**
  - **Traditionally attributed to oxygen vacancies**



- **First-principles calculations:**
  - **oxygen vacancies are *not* shallow donors!**
  - **So what is the cause?…**

Hydrogen in ZnO





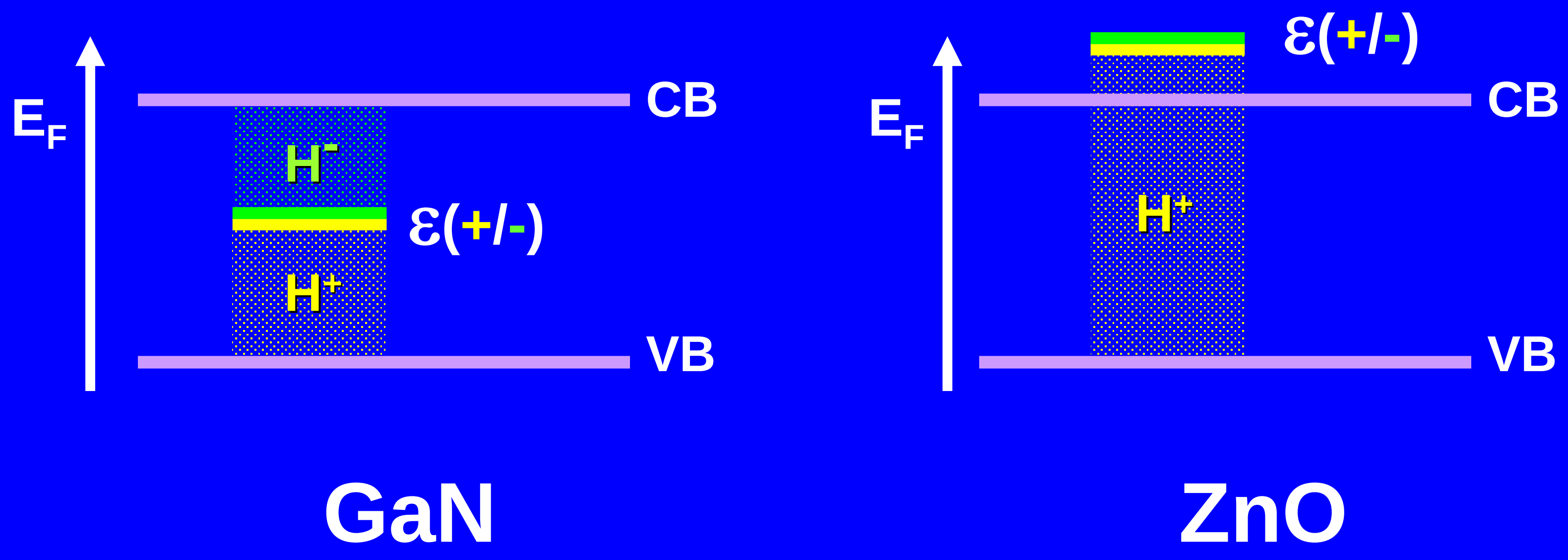
H^+ is the only stable charge state

Phys. Rev. Lett. **85**, 1012 (2000)

Confirmed by more than 20 experiments to date

Why is ZnO different?

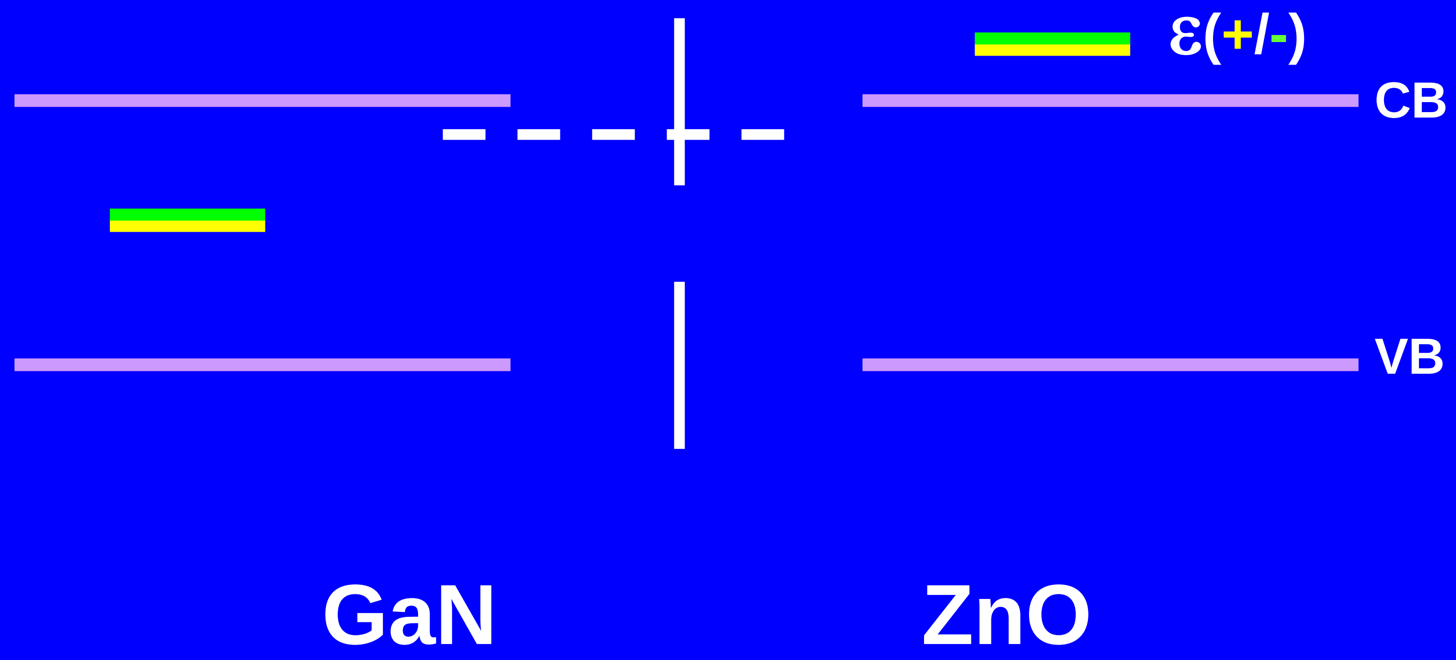
- Position of ε(+/-) in the band gap



- Question: Why is ε(+/-) so much higher in energy in ZnO?

Why is ZnO different?

Band lineups!



Why is ZnO different?

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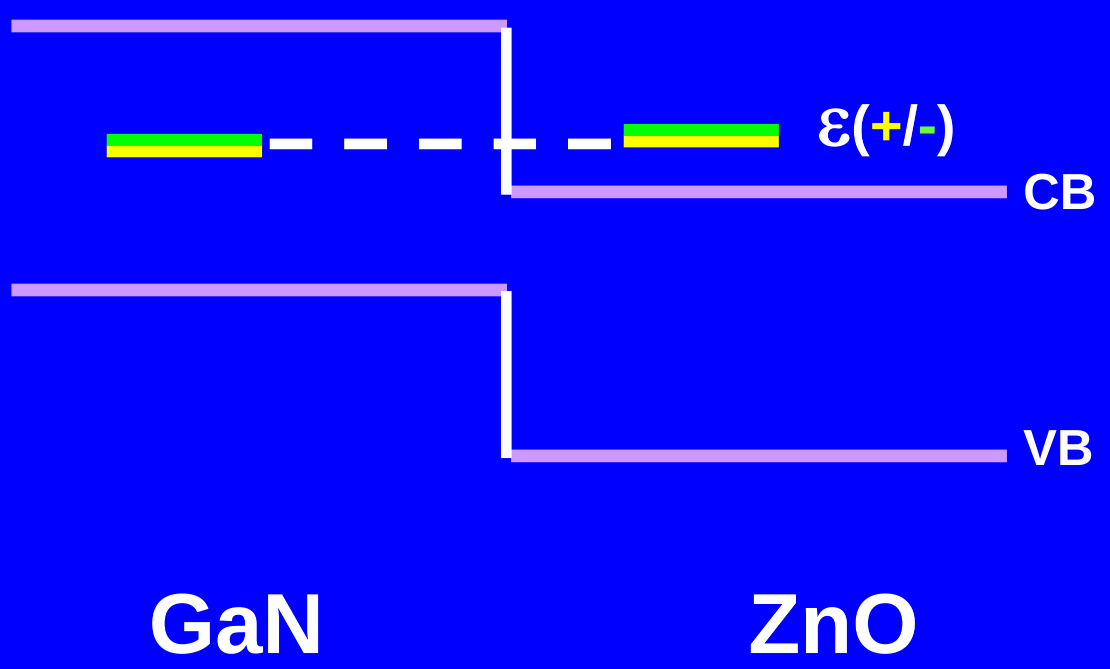
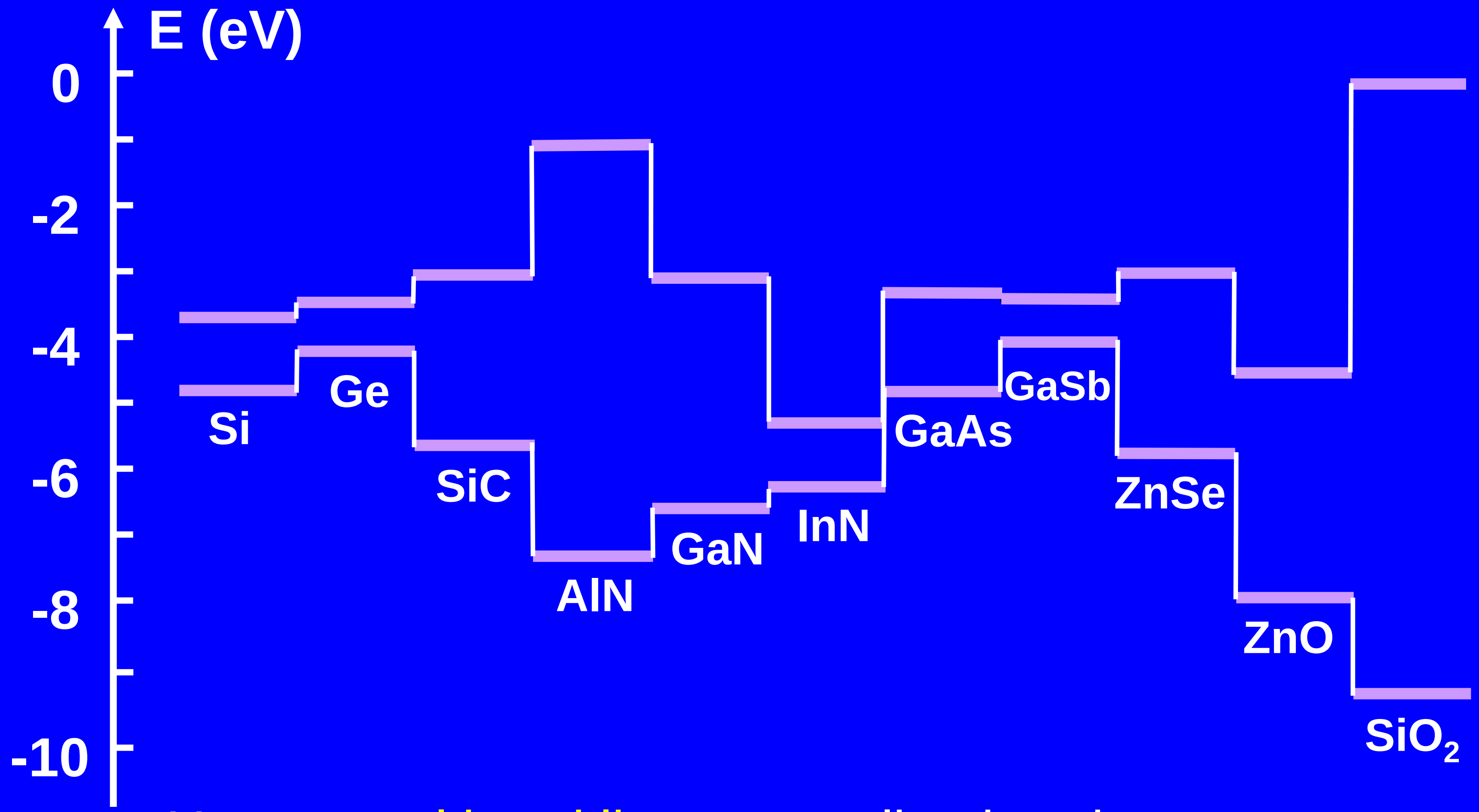


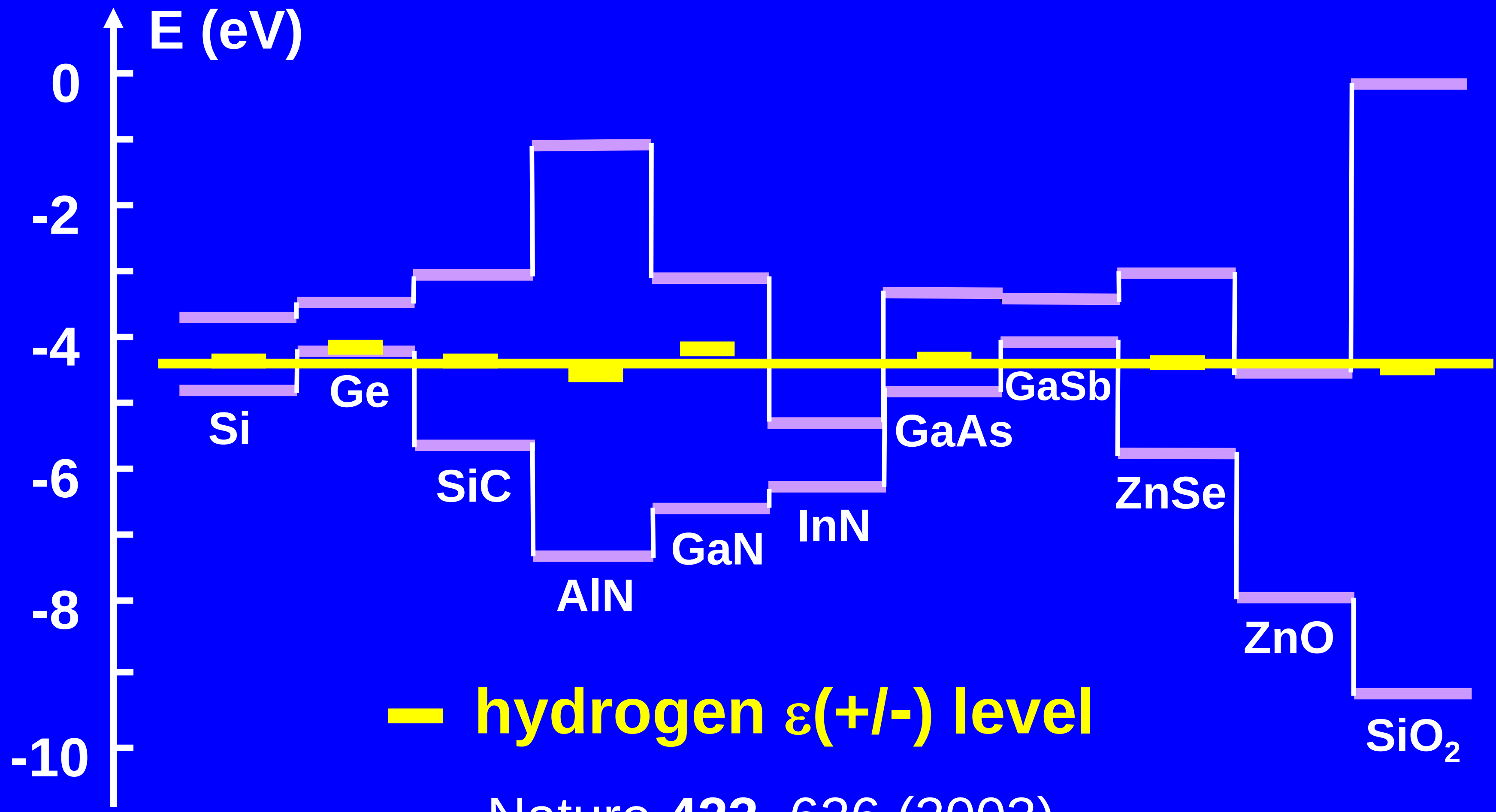
Band lineups



Use natural band lineups to align band structures

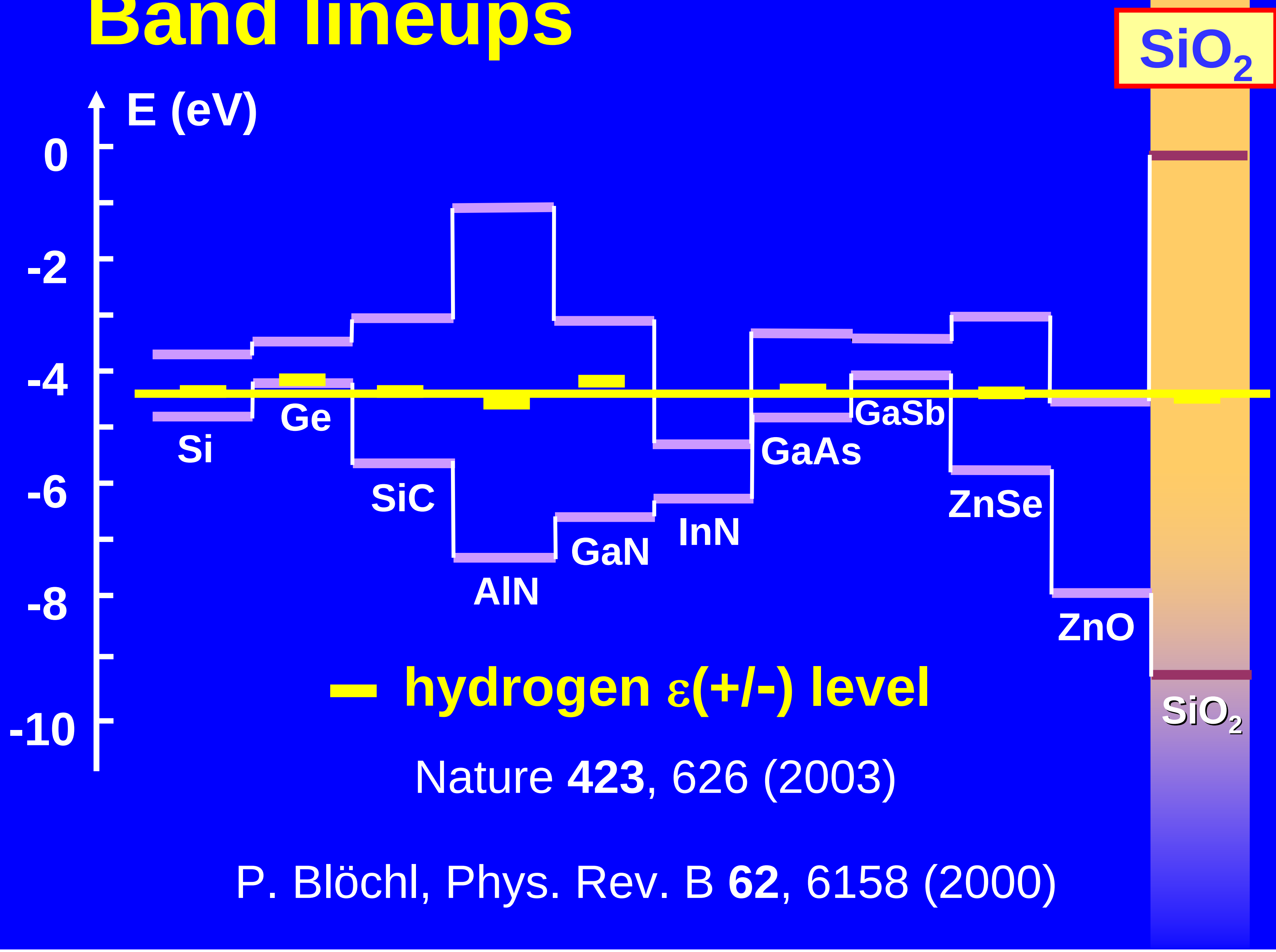
C. G. Van de Walle, Phys. Rev. B **39**, 1871 (1989)

Band lineups



Nature **423**, 626 (2003)

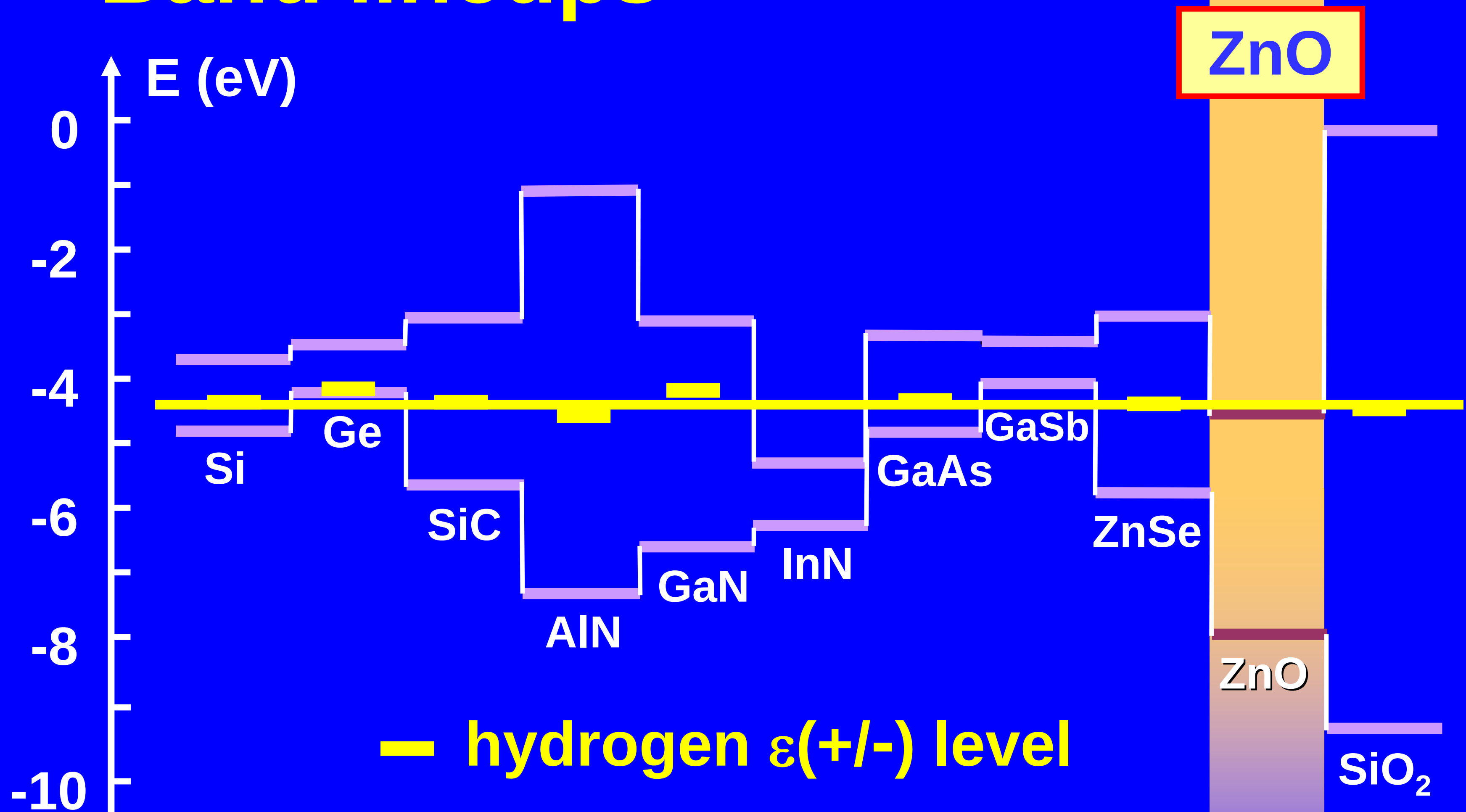
Band lineups



Nature **423**, 626 (2003)

P. Blöchl, Phys. Rev. B **62**, 6158 (2000)

Band lineups



Nature **423**, 626 (2003)

C. G. Van de Walle, Phys. Rev. Lett. **85**, 1012 (2000)

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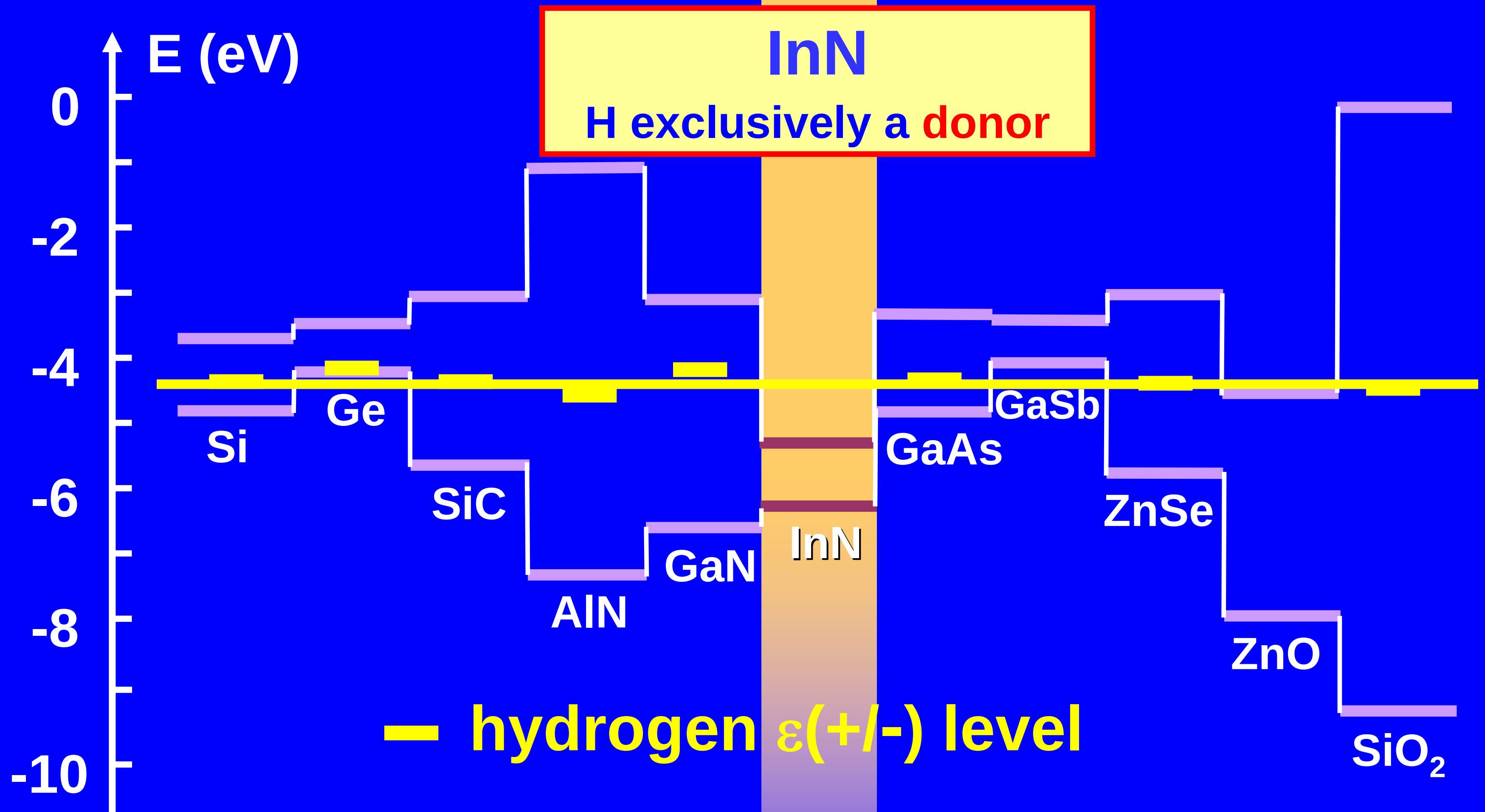
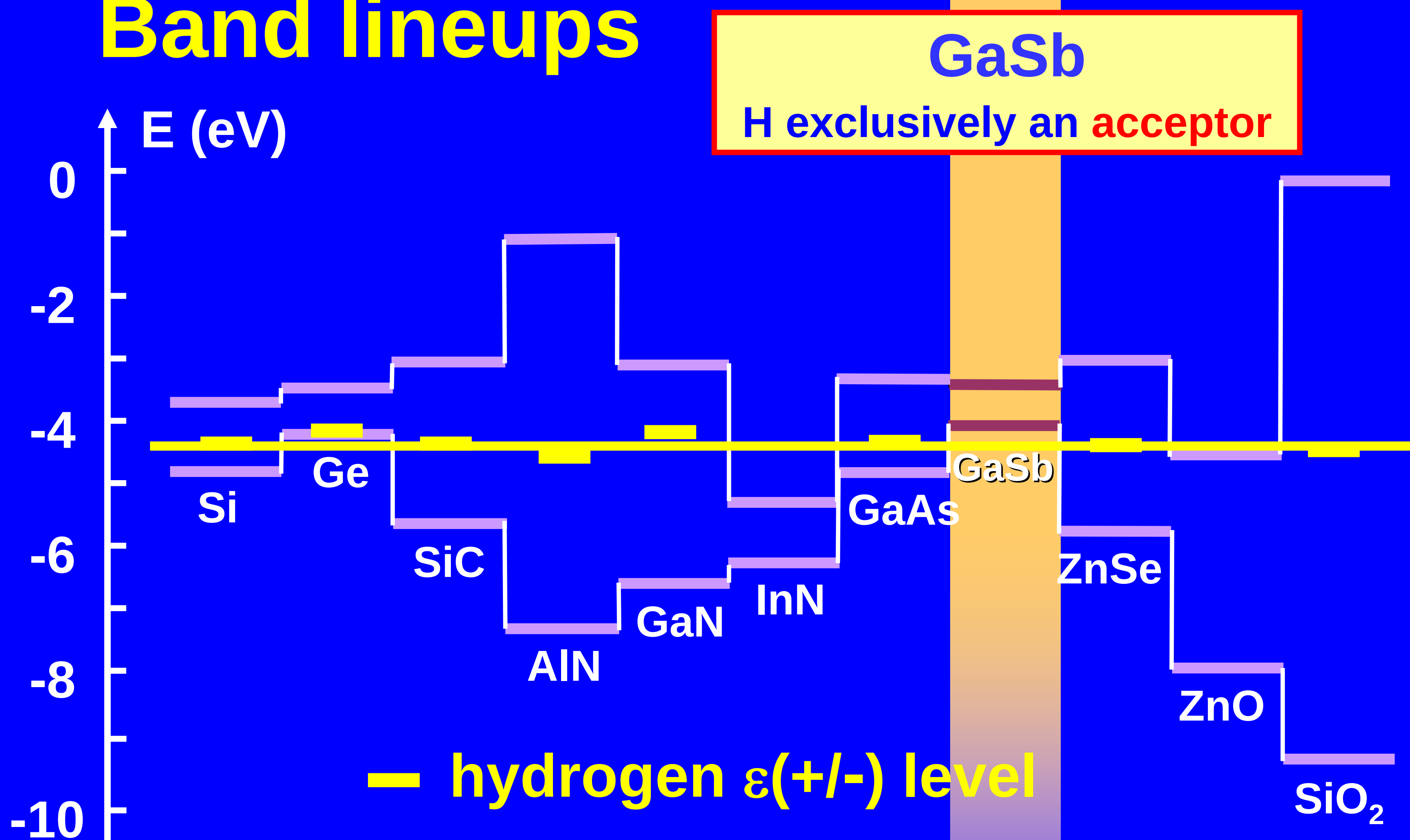


Nature **423**, 626 (2003)

Experiment: Appl. Phys. Lett. **82**, 592 (2003).

Band lineups



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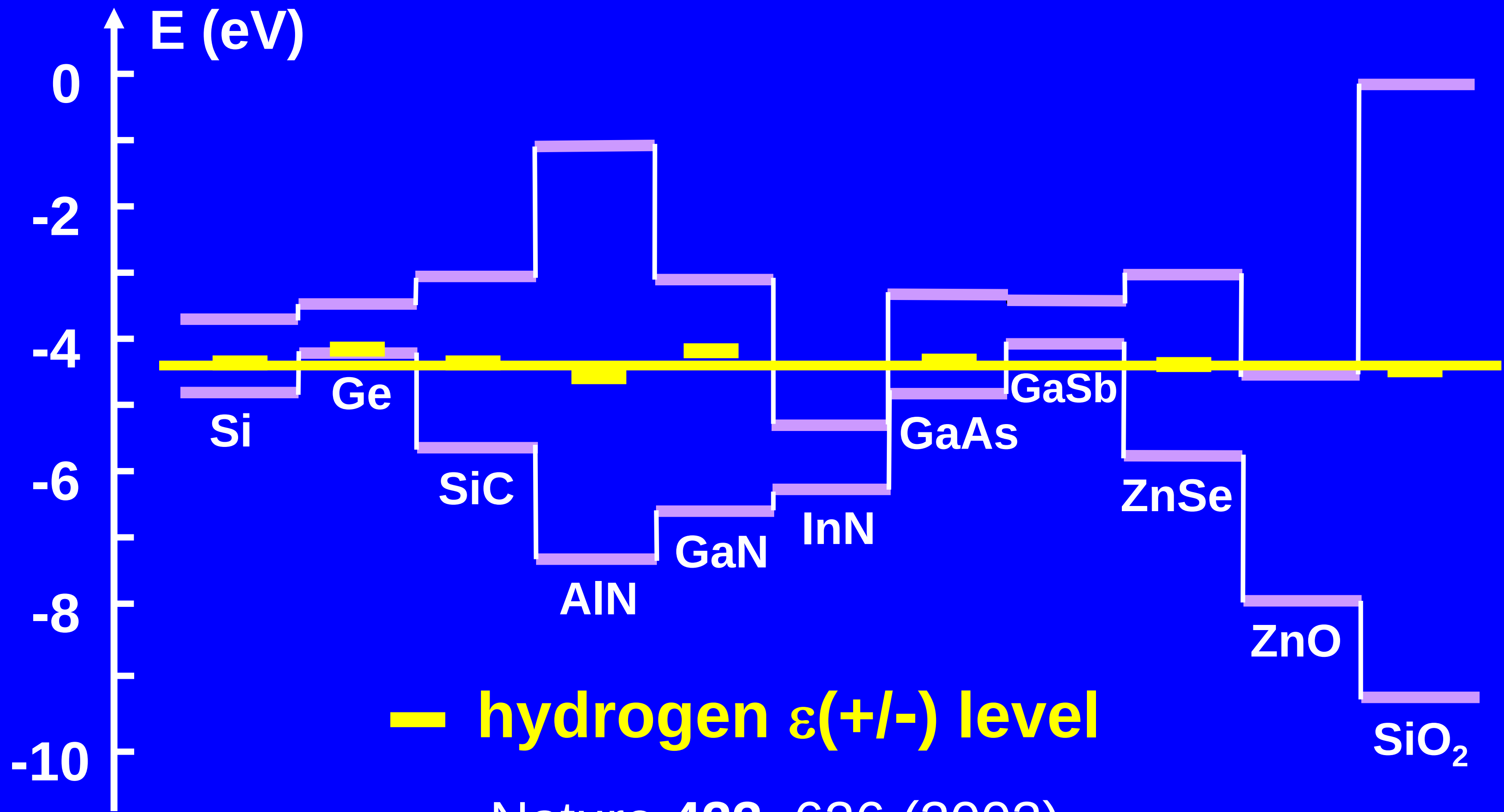

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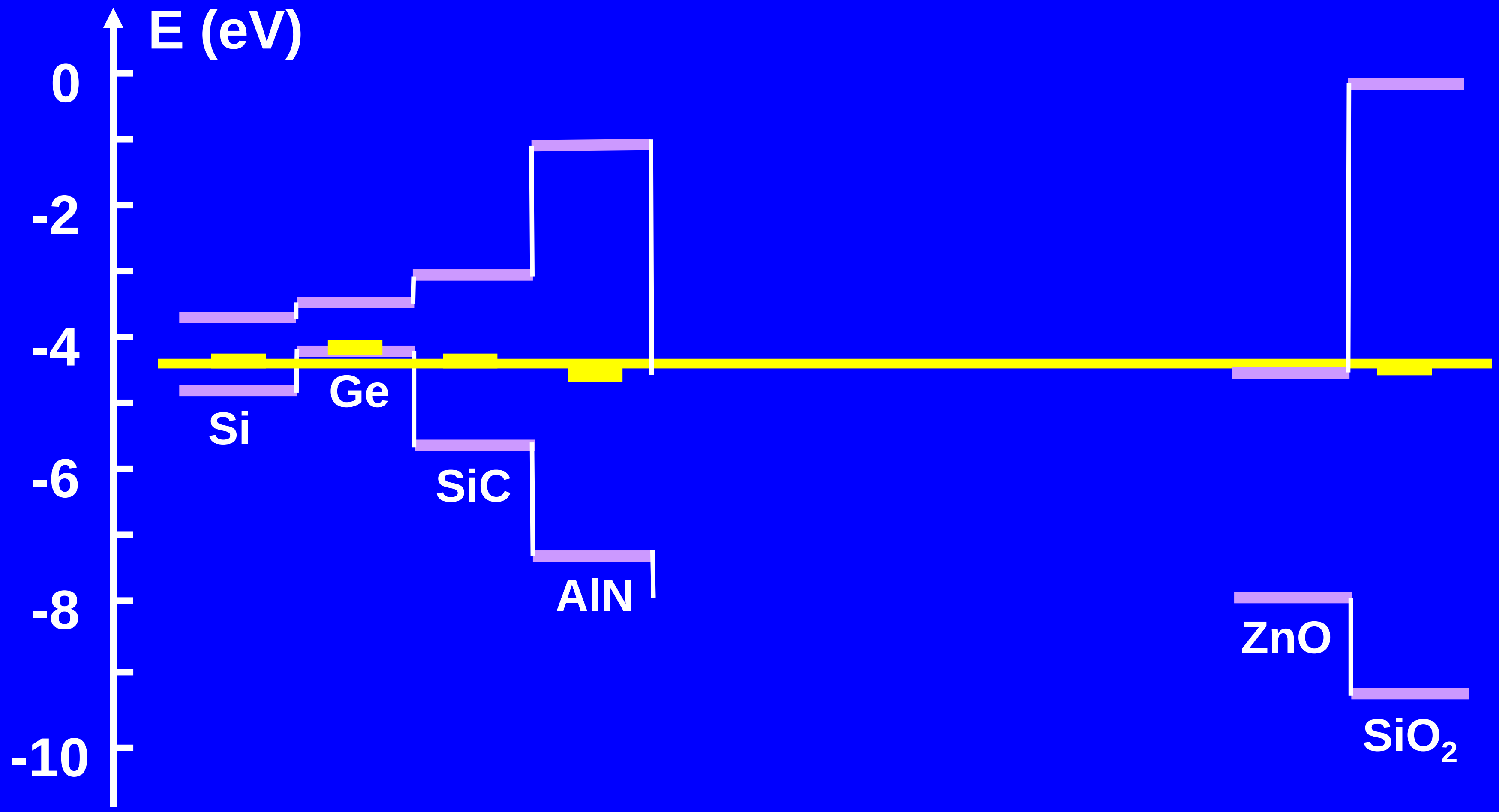

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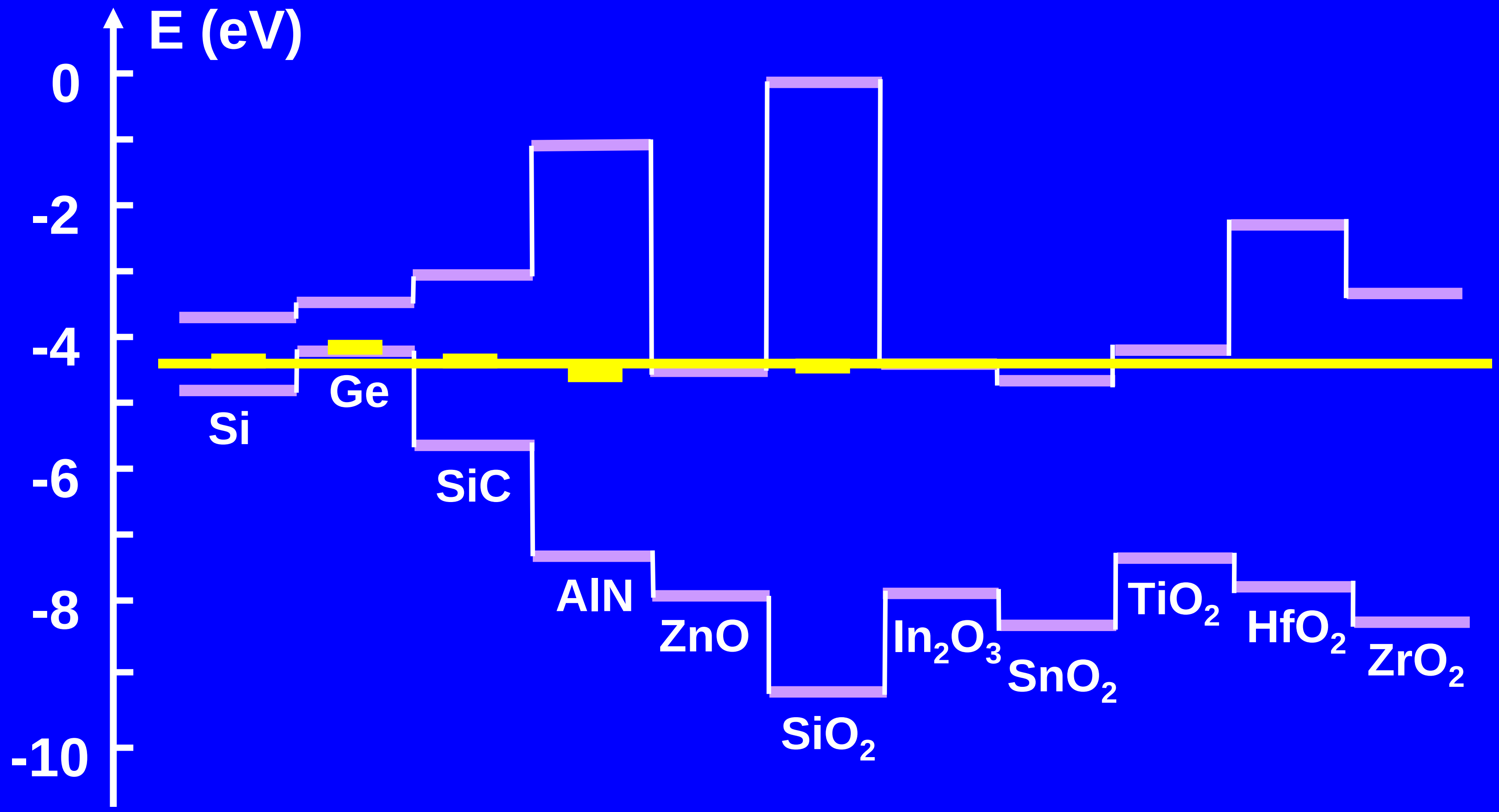
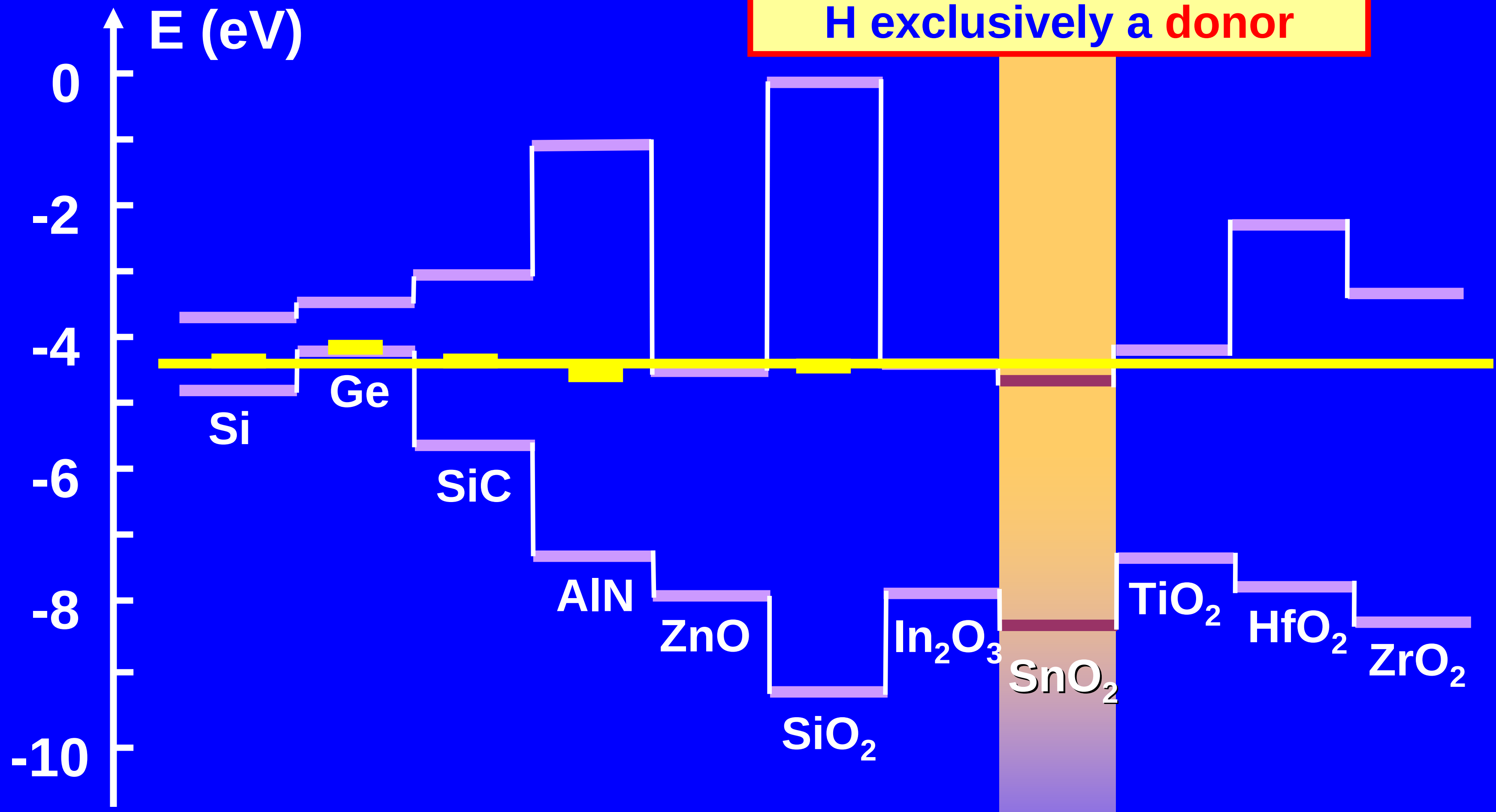


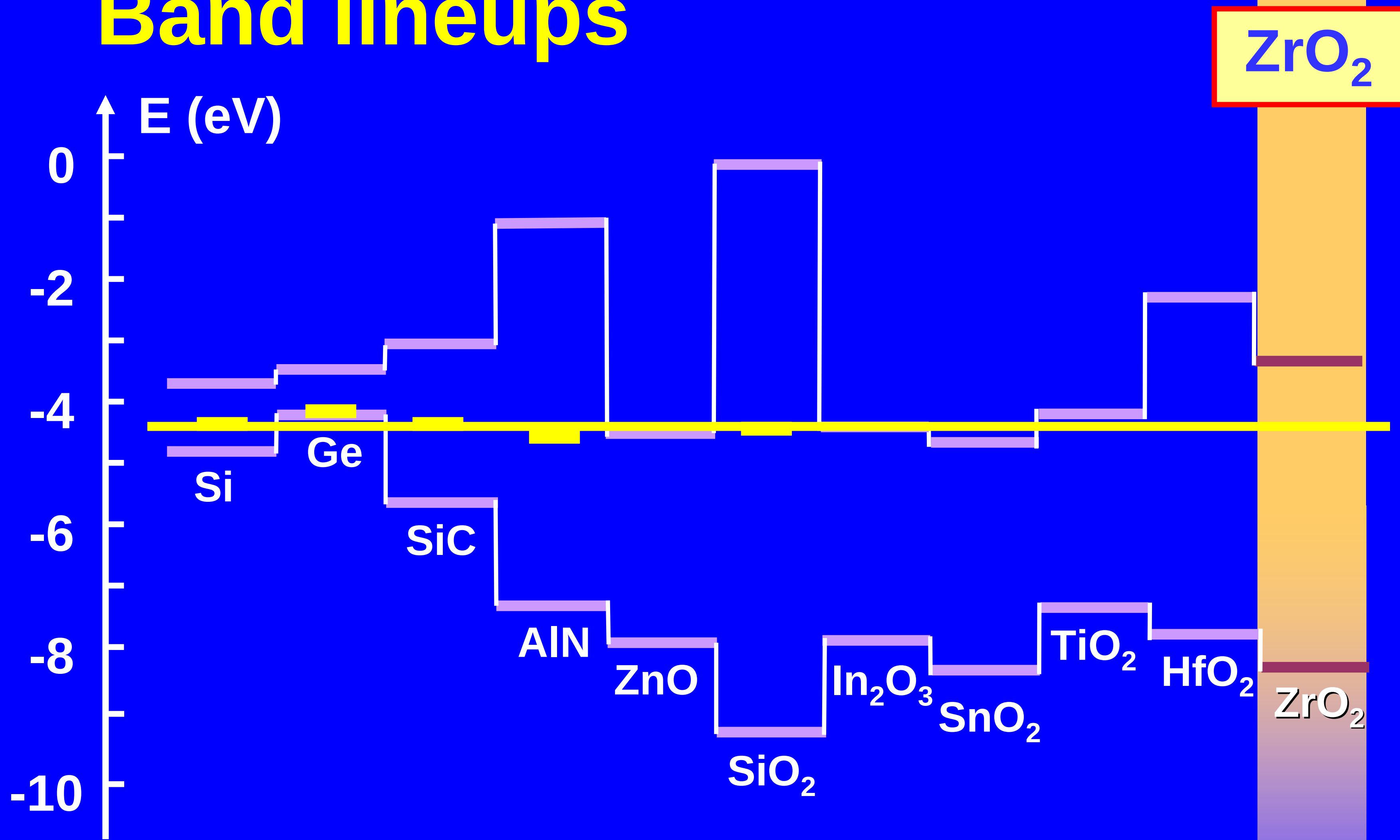
Band lineups

SnO_2
H exclusively a donor



Transparent conductors

Band lineups



High-k dielectrics

Conclusions

- Hydrogen strongly interacts with defects and impurities
- Understanding this behavior:
  - First-principles calculations
- Interstitial hydrogen:
  - basis for understanding complex interactions
- Towards general understanding:
  - Universal alignment
  - Predictive model
- Connection with band lineups