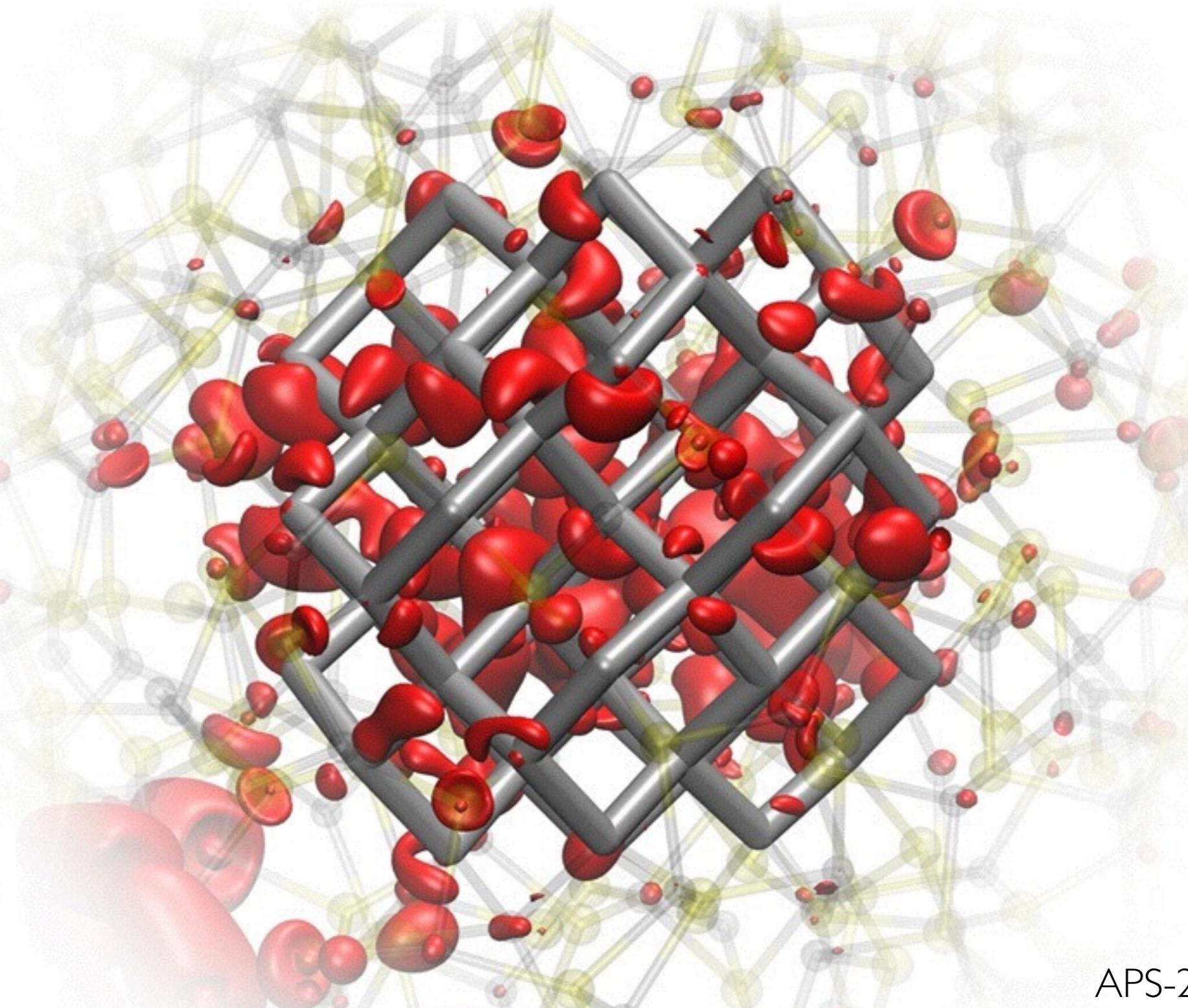




High pressure phase Ge nanoparticles and Si-ZnS nanocomposites: new paradigms to improve the efficiency of MEG solar cells



S. Wippermann, M. Vörös, B. Somogyi, D. Rocca, A. Gali, G. Zimanyi, F. Gygi, G. Galli



MAX-PLANCK-GESELLSCHAFT

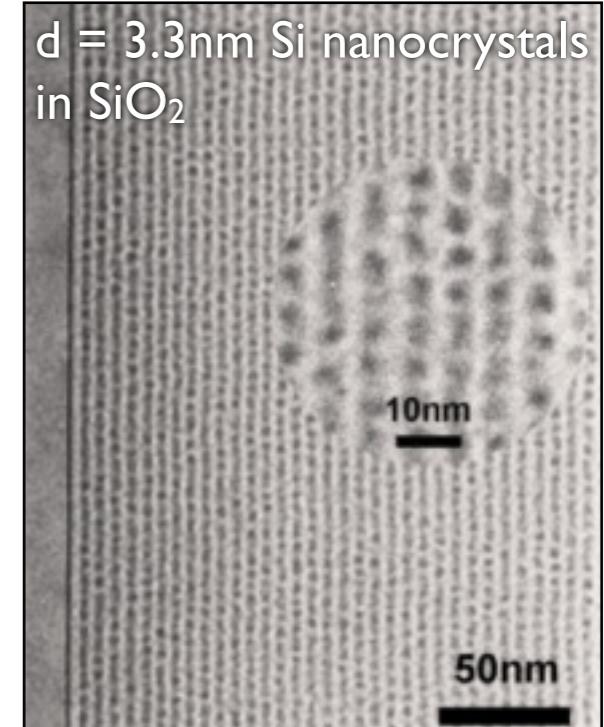
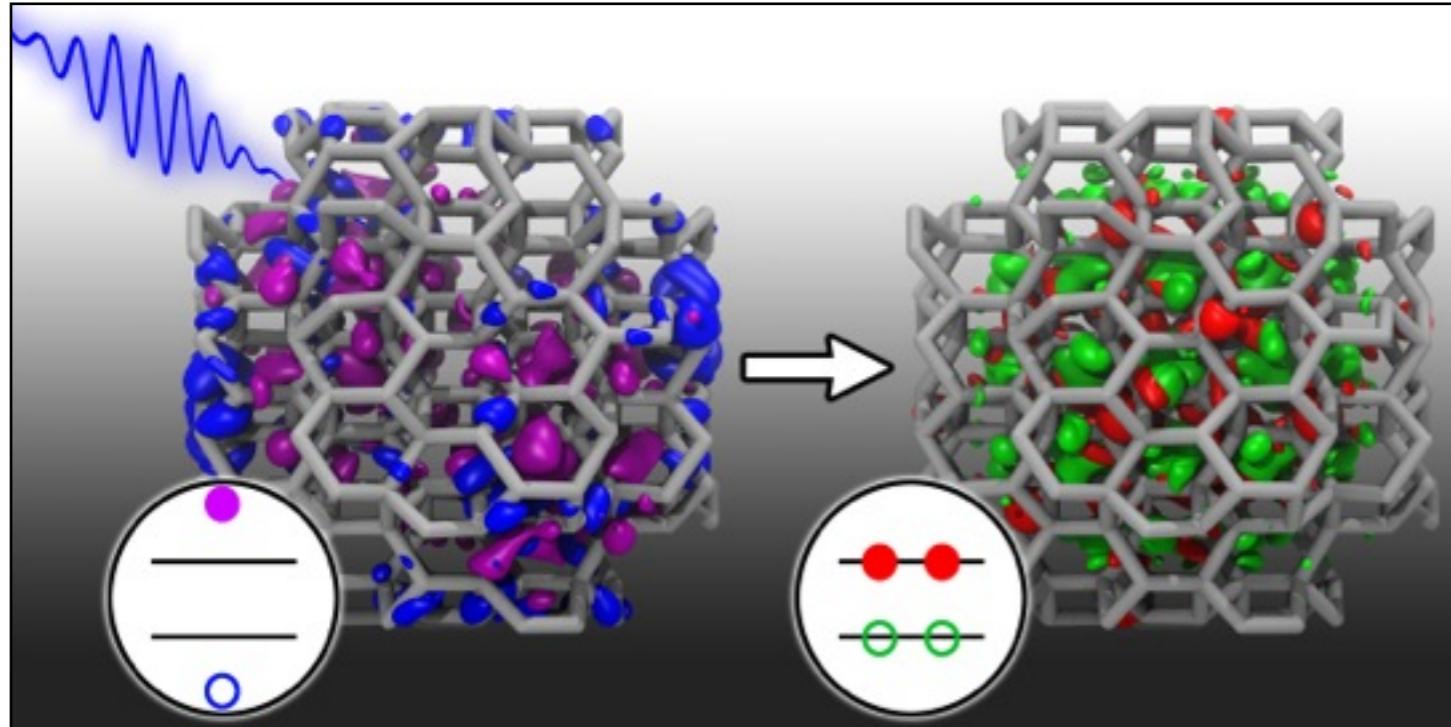


NanoMatFutur



APS-2014, 03/05/2014

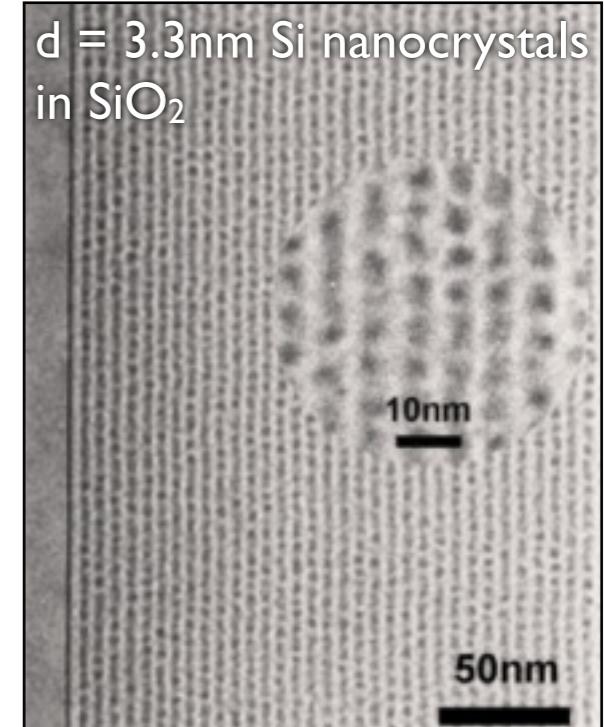
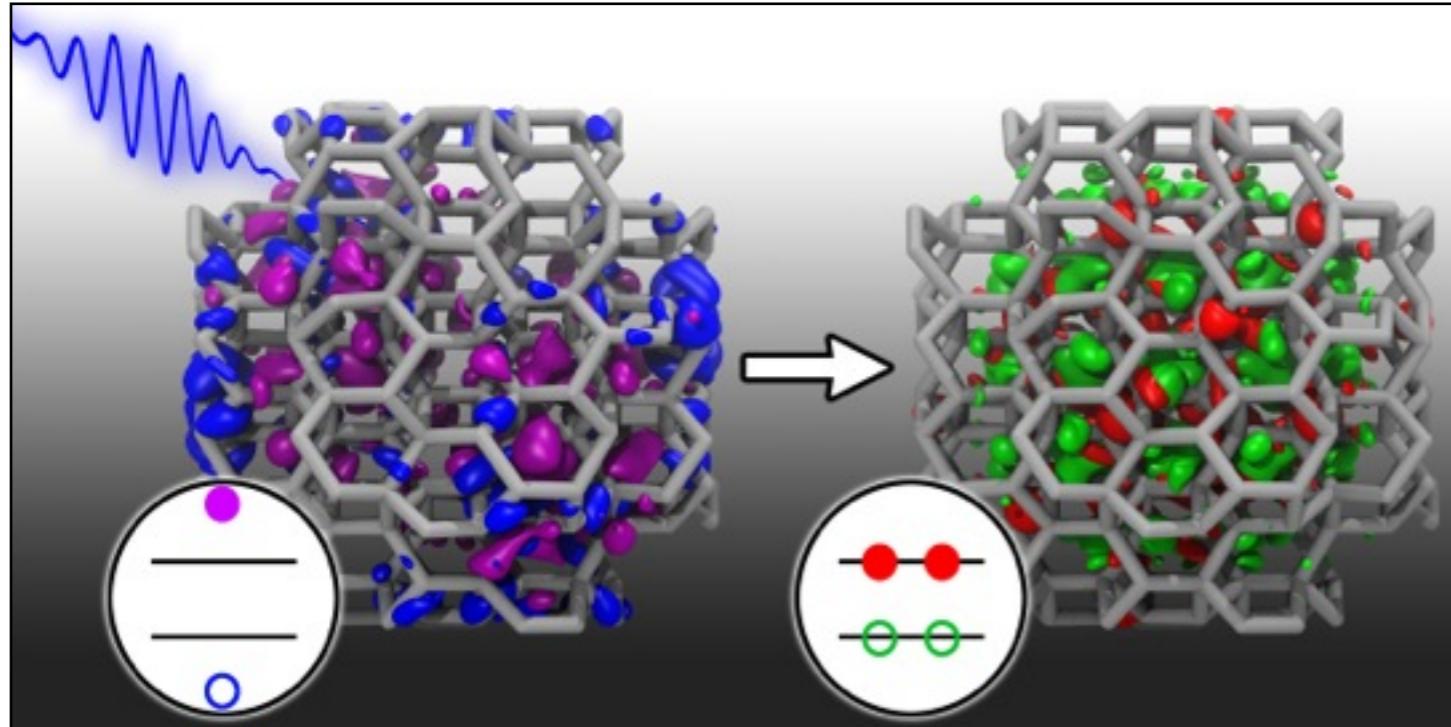
Multiple Exciton Generation (MEG)



[M. Zacharias et al., Appl. Phys. Lett. **80**, 661 (2002)]

- ➊ **MEG:** hot exciton relaxes by exciting another exciton
- ➋ enhanced MEG in quantum-confined nanostructures, e. g. nanocrystals

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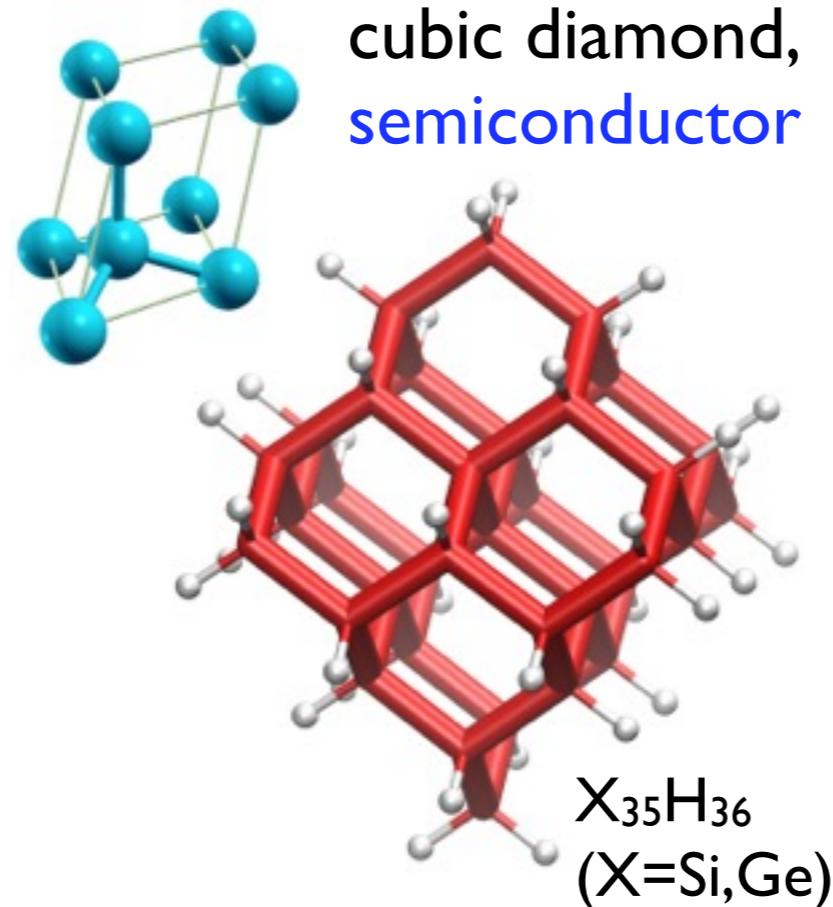
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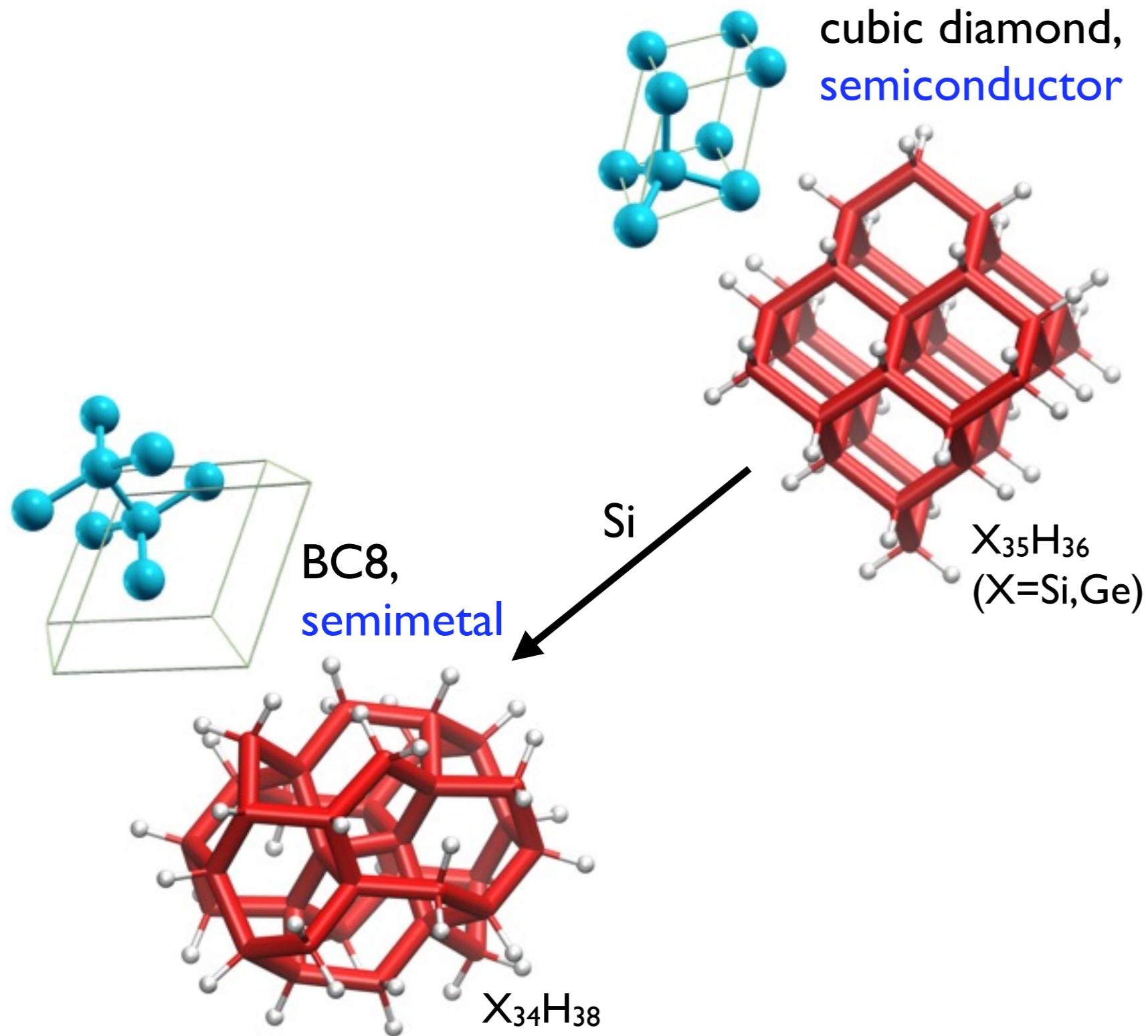
Key problems

- ➊ Quantum confinement required for efficient MEG, but pushes electronic gap beyond solar spectrum
- ➋ Ensure efficient charge transport & extraction and low recombination rates

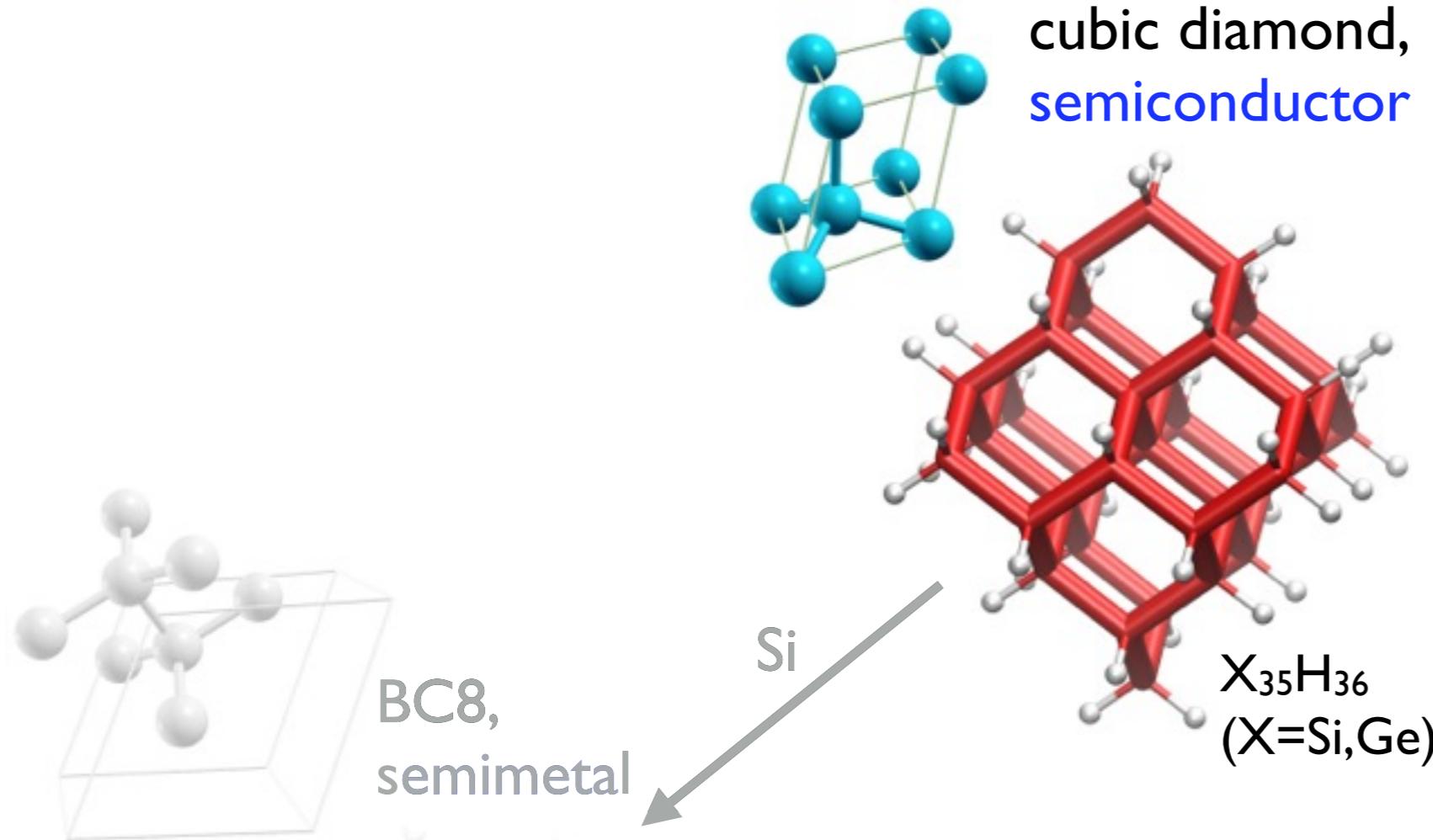
Allotropes of Si and Ge



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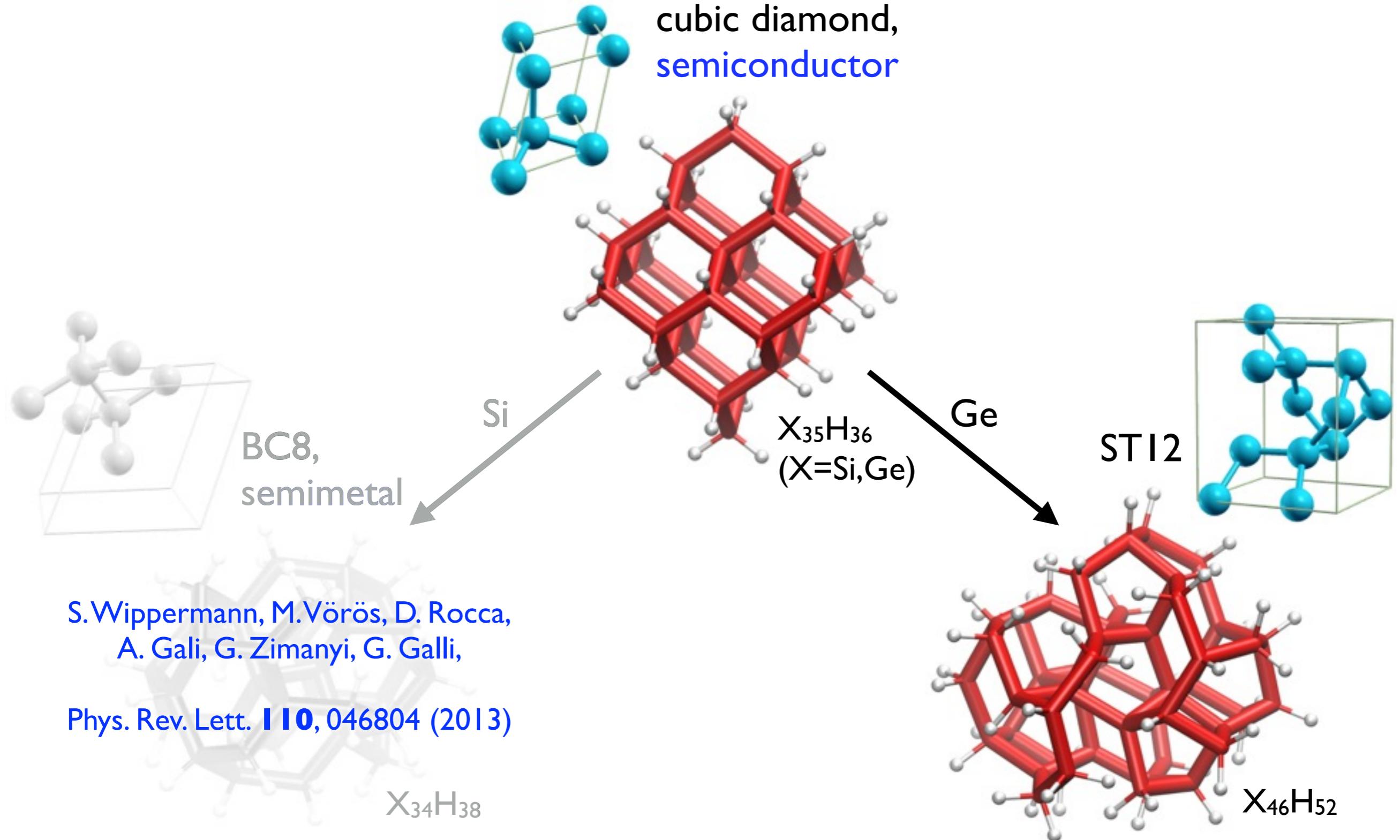


S. Wippermann, M. Vörös, D. Rocca,
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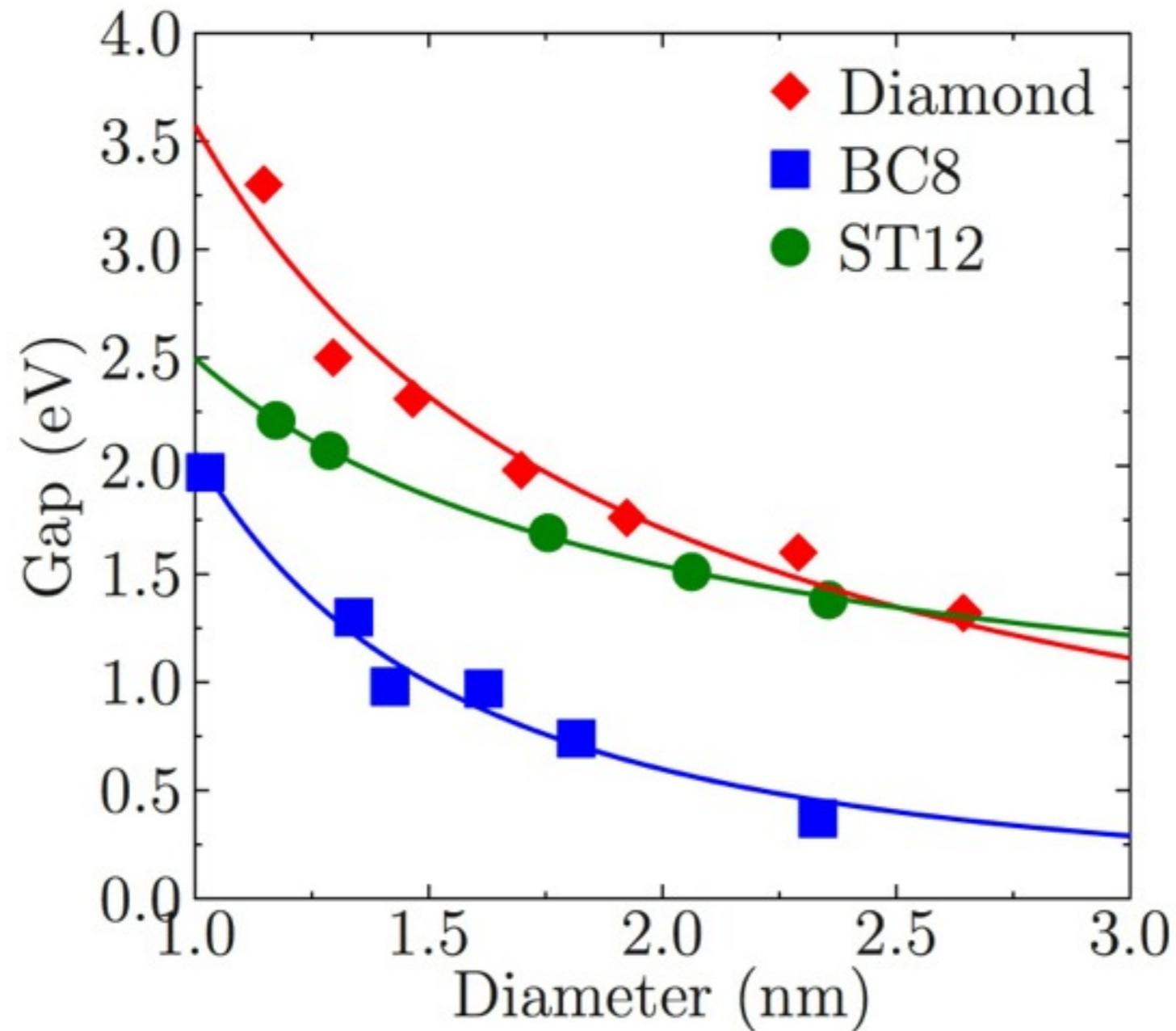
Phys. Rev. Lett. **110**, 046804 (2013)

$X_{34}H_{38}$

Allotropes of Si and Ge



Electronic gaps of Ge allotrope nanocrystals

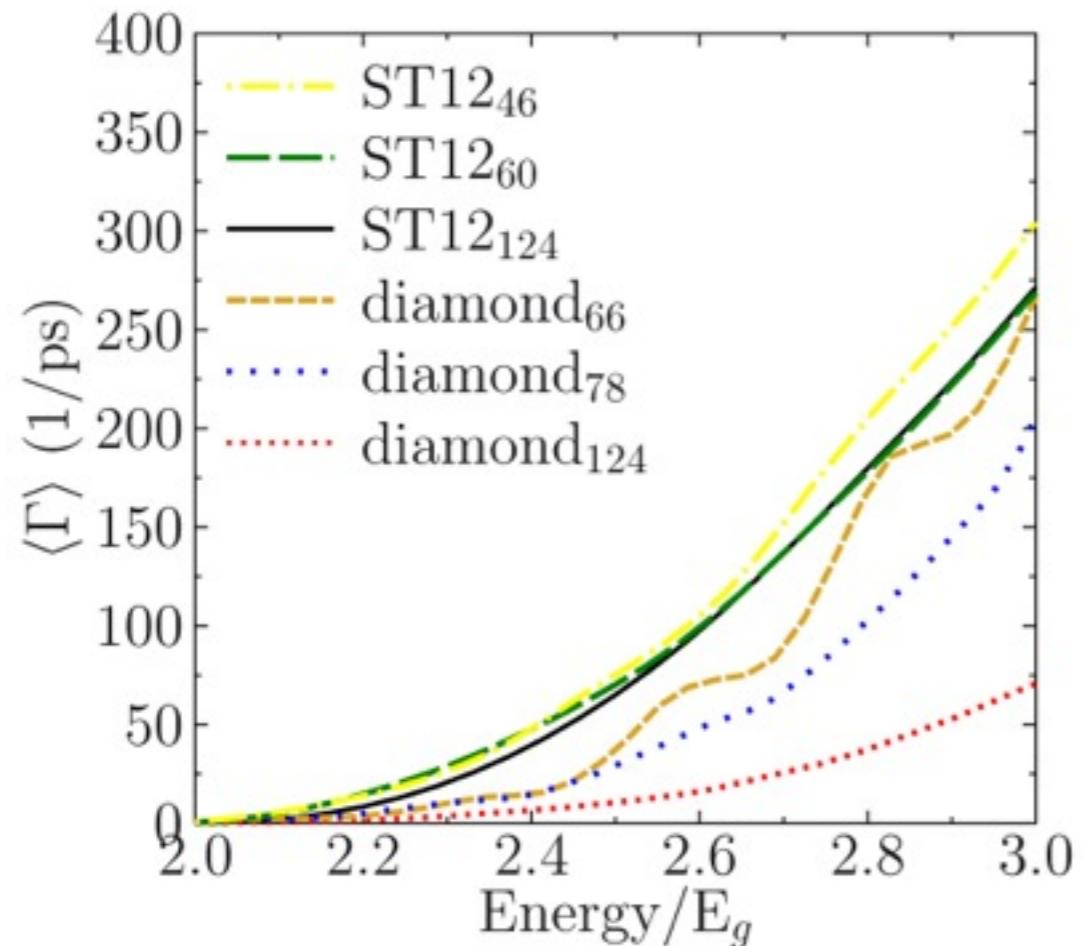


Density Functional Theory (DFT) calculations show smaller electronic gaps for Ge ST12 nanocrystals, compared to cubic diamond Ge nanocrystals, for $d < 2.5$ nm



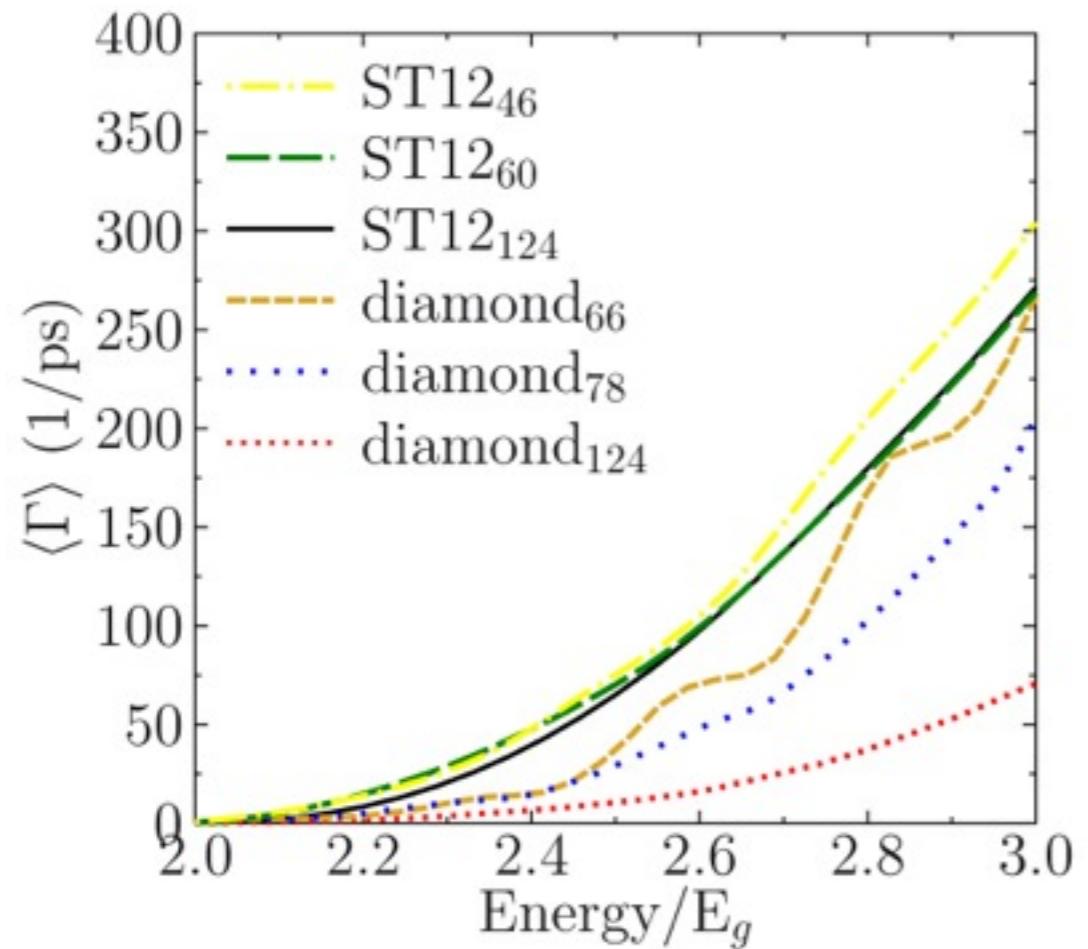
even lower gaps for Ge BC8, but only stable for Si and not Ge

Multiple Exciton Generation in Ge allotrope nanocrystals



Impact ionization (II) is dominating contribution to MEG; calculate II rates from *first principles* [M.Vörös, D. Rocca, G. Galli, G. Zimanyi, A. Gali, PRB **87**, 155402 (2013)]

Multiple Exciton Generation in Ge allotrope nanocrystals

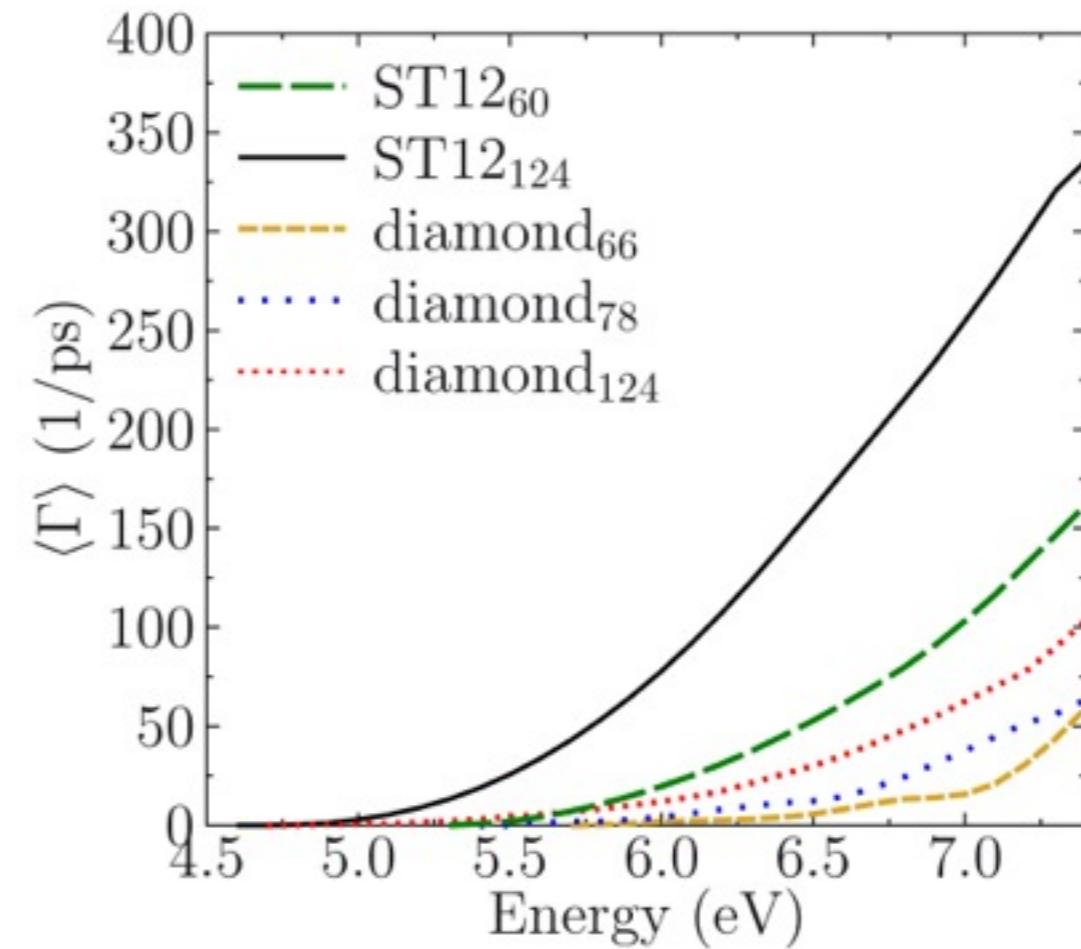
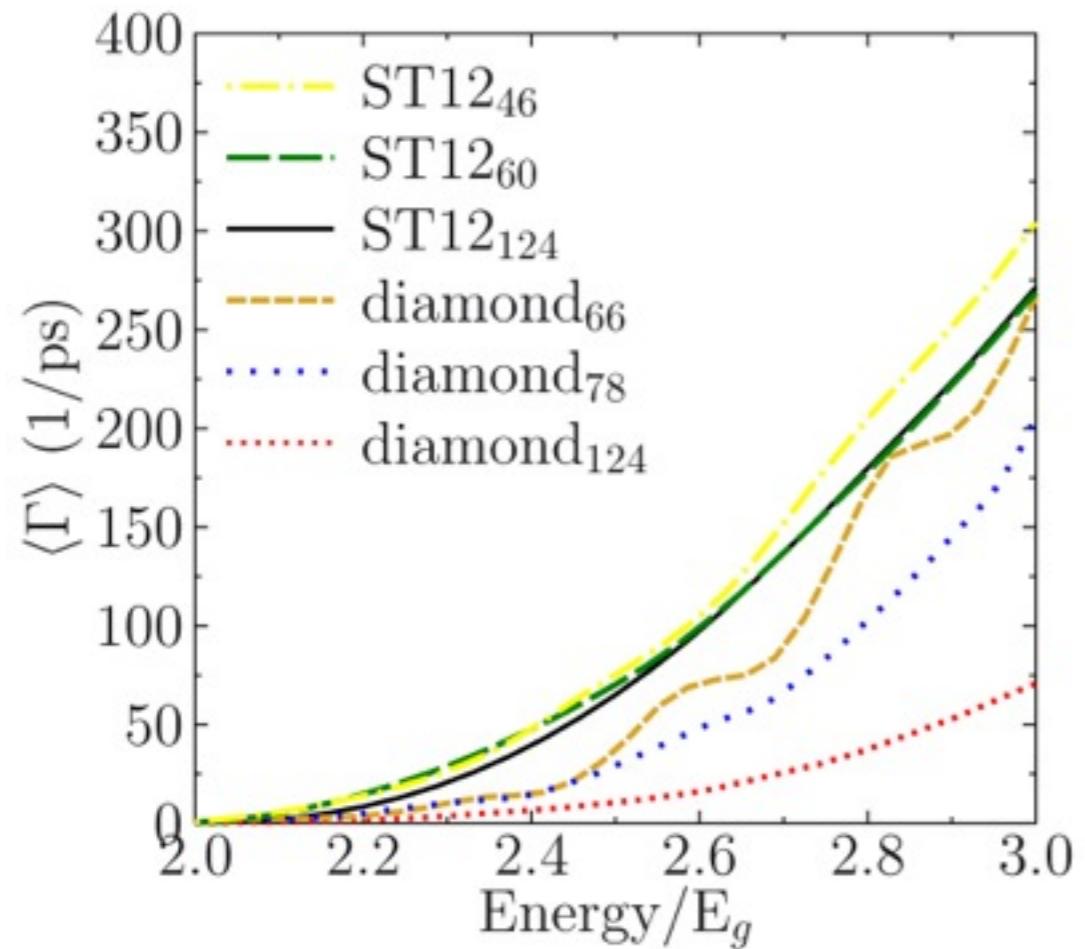


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ST12 II rates size-independent

Increasing EDOS at band edges counterbalances loss of confinement

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Increasing EDOS at band edges counterbalances loss of confinement



Simultaneously lower electronic gaps and higher relative II efficiency translate to significantly improved MEG on absolute energy scale

Intermediate summary

- Simple structural change at constant size and number of atoms yields solid improvement on all fronts
- Proposal: Electronic gap vs. quantum confinement dilemma is in fact a trilemma, involving electronic density of states (EDOS) at band edges*
- Experimentally testable, Ge STI2 nanocrystals can be synthesized in solution

M.Vörös, S.Wippermann, B. Somogyi, A. Gali, D. Rocca, G. Galli, G. Zimanyi (under review)

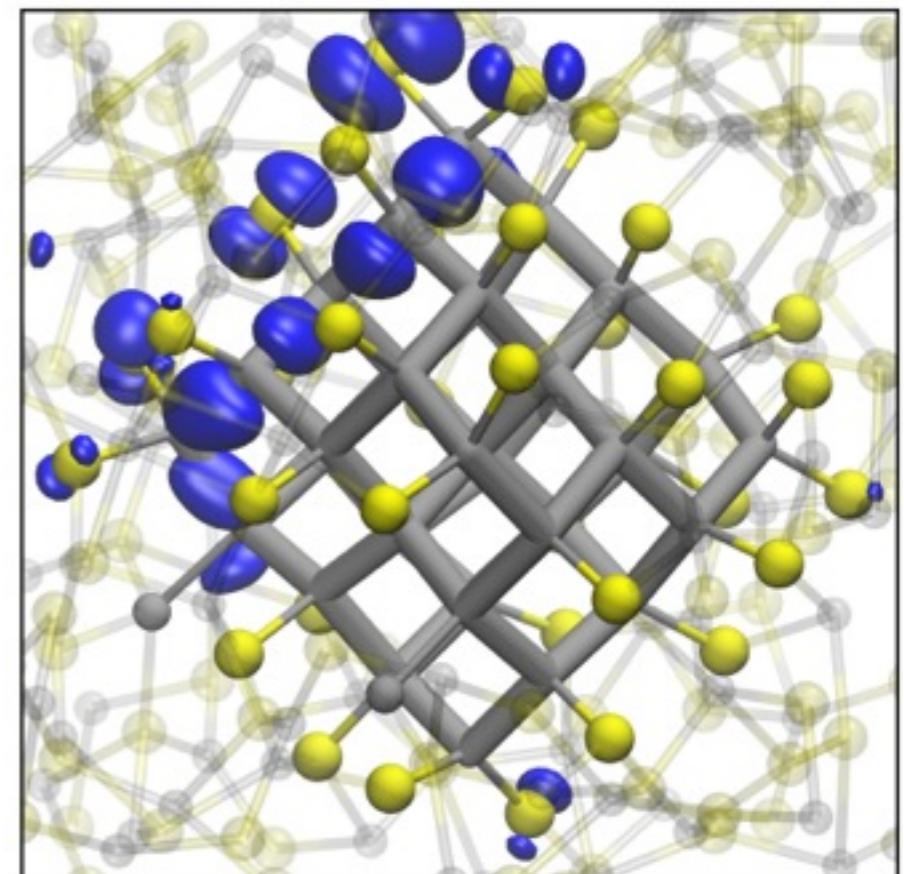
Outline

Key problems

- ➊ Quantum confinement required for efficient MEG, but pushes electronic gap beyond solar spectrum
- ➋ Ensure efficient charge transport & extraction and low recombination rates

Si nanocrystals embedded in a-ZnS

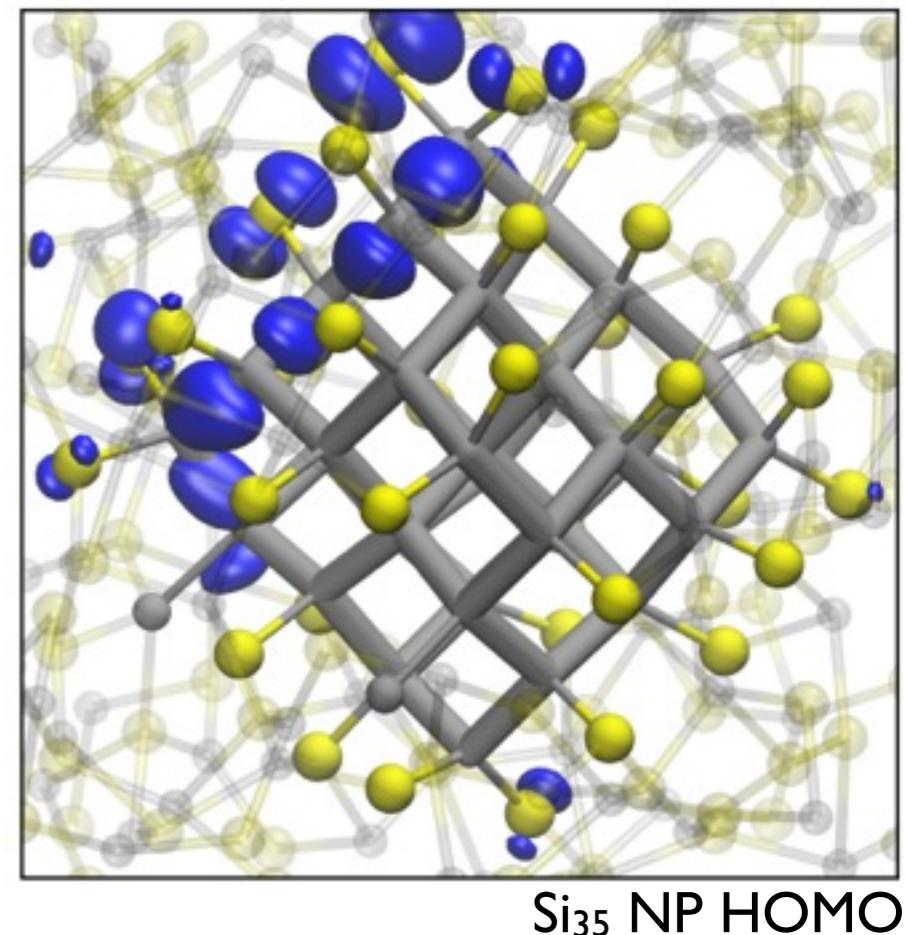
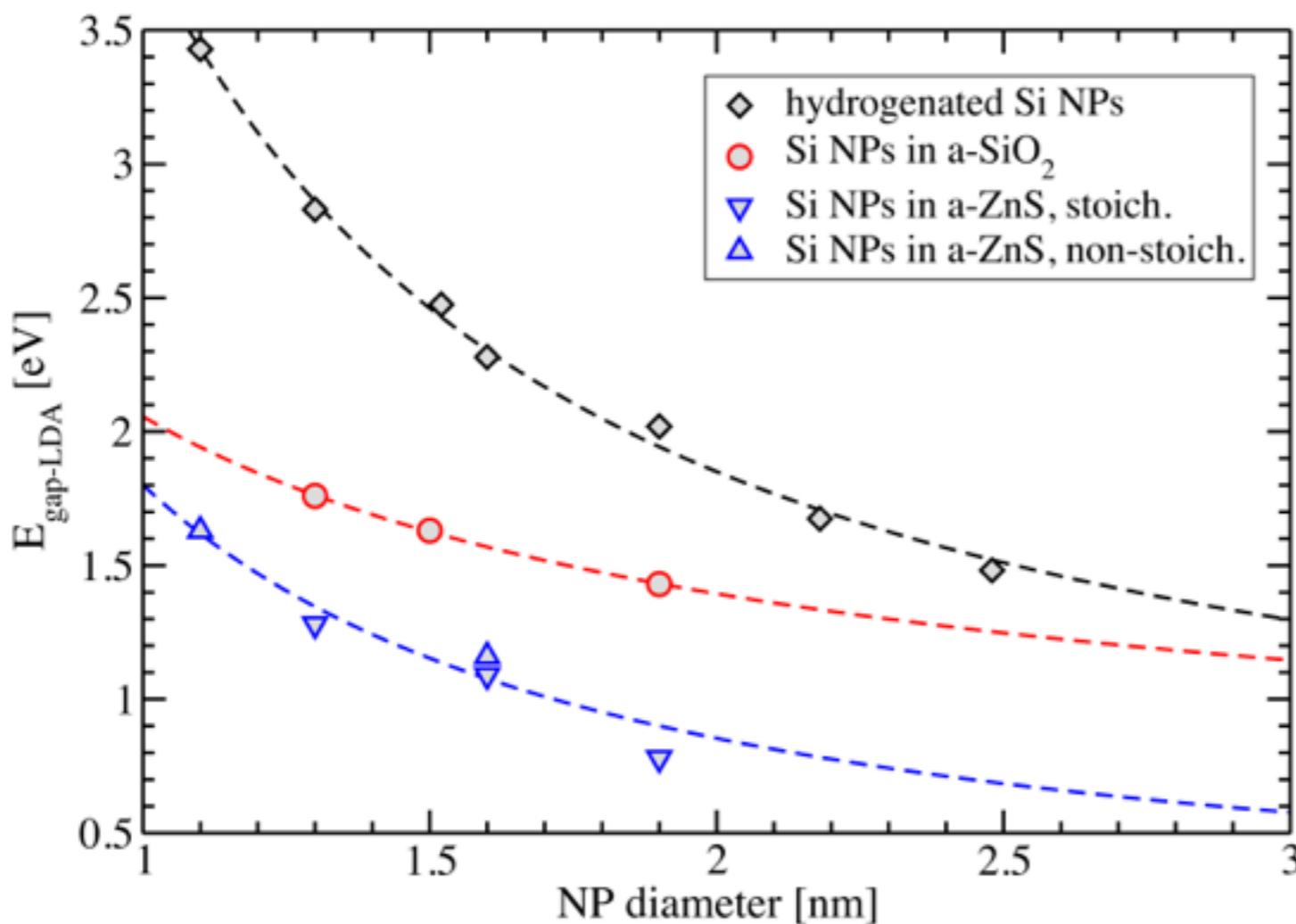
- >Create structural models for a-ZnS embedded **Si₃₅, Si₆₆, Si₁₂₃, Si₁₇₂** nanoparticles (NPs) from *ab initio* molecular dynamics (MD)



Si₃₅ NP HOMO

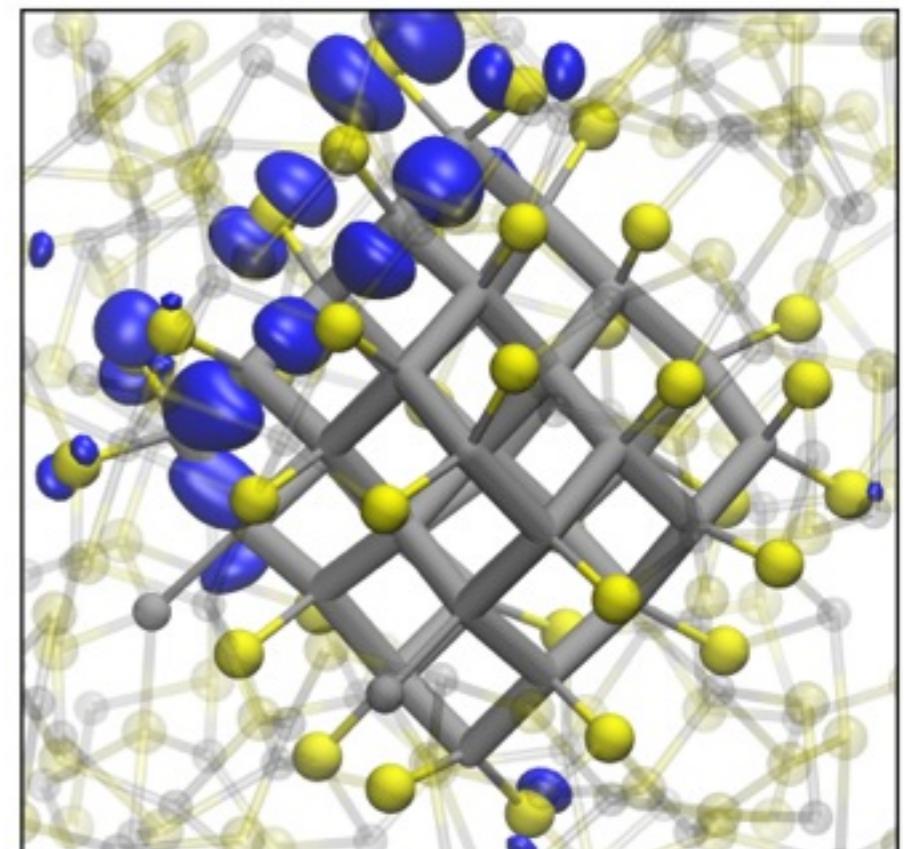
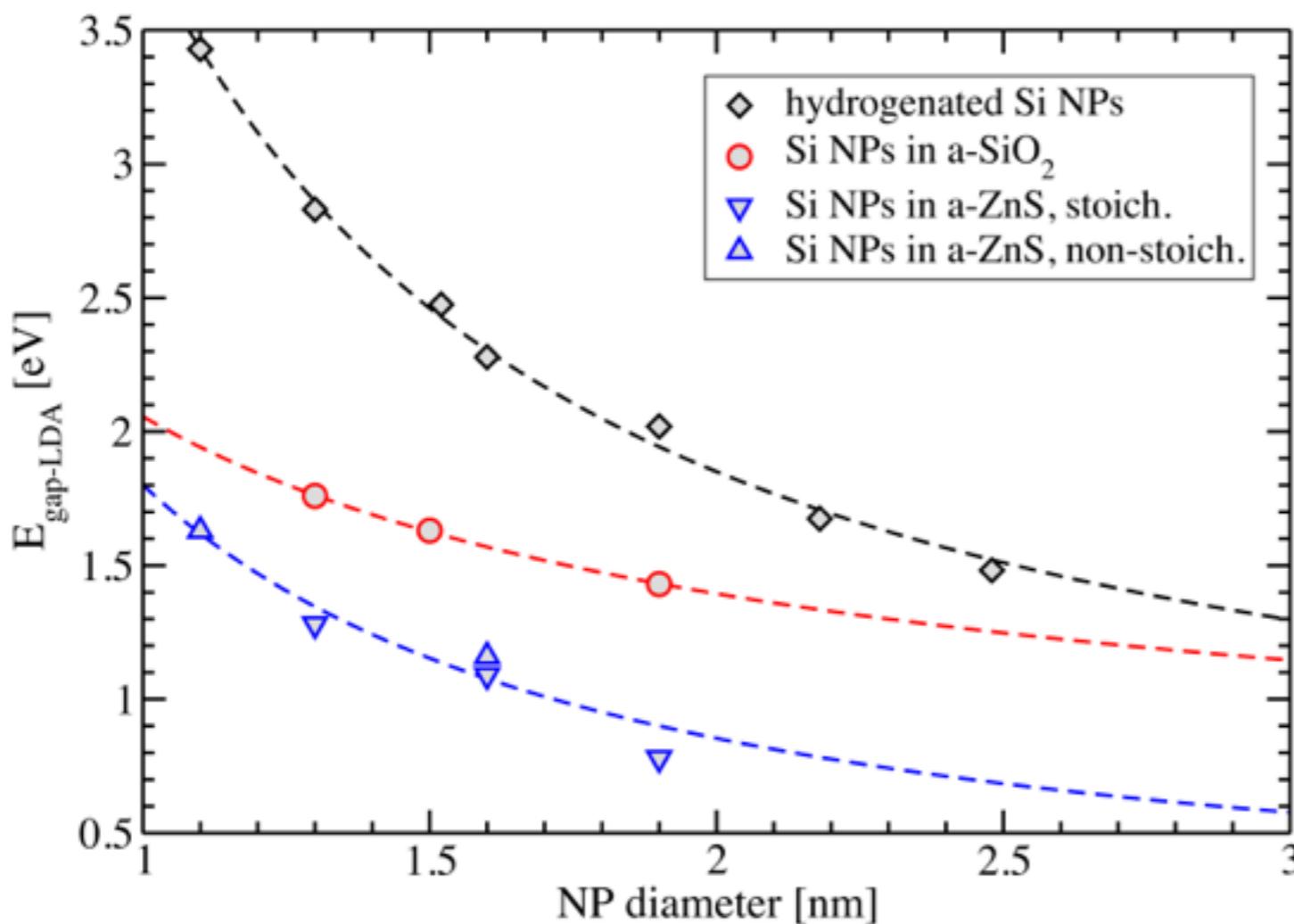
Si nanocrystals embedded in a-ZnS

- >Create structural models for a-ZnS embedded Si_{35} , Si_{66} , Si_{123} , Si_{172} nanoparticles (NPs) from *ab initio* molecular dynamics (MD)
- Pronounced gap reduction of embedded NPs due to sulfur shell formation

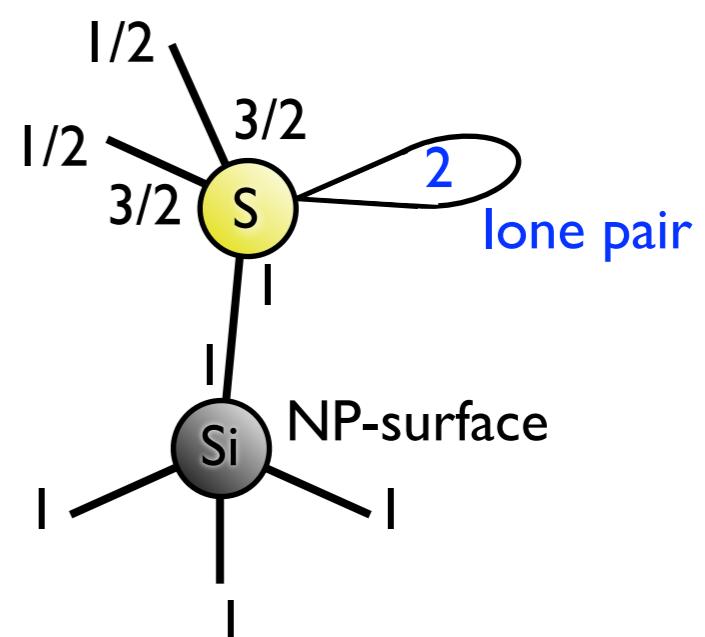


Si nanocrystals embedded in a-ZnS

- >Create structural models for a-ZnS embedded Si_{35} , Si_{66} , Si_{123} , Si_{172} nanoparticles (NPs) from *ab initio* molecular dynamics (MD)
- Pronounced gap reduction of embedded NPs due to sulfur shell formation
- Lone pairs of 3-fold coordinated sulfur at NP-matrix interface introduce new occupied mid-gap states

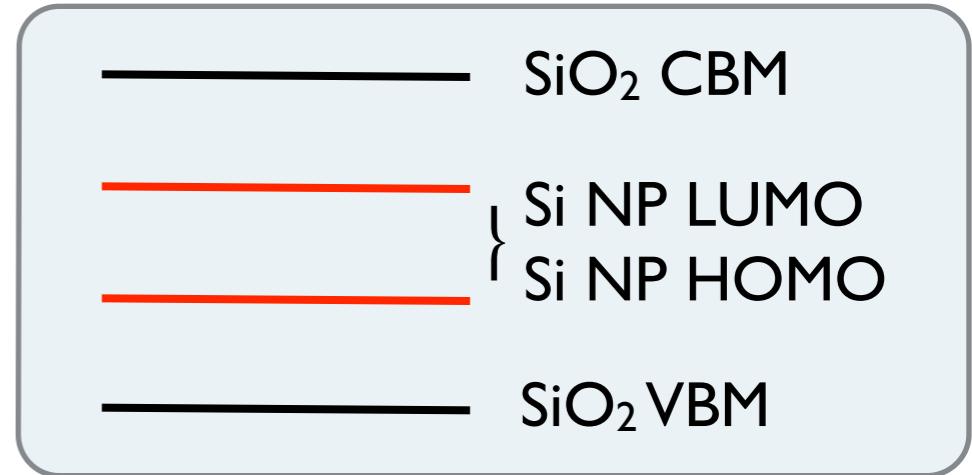


Si_{35} NP HOMO

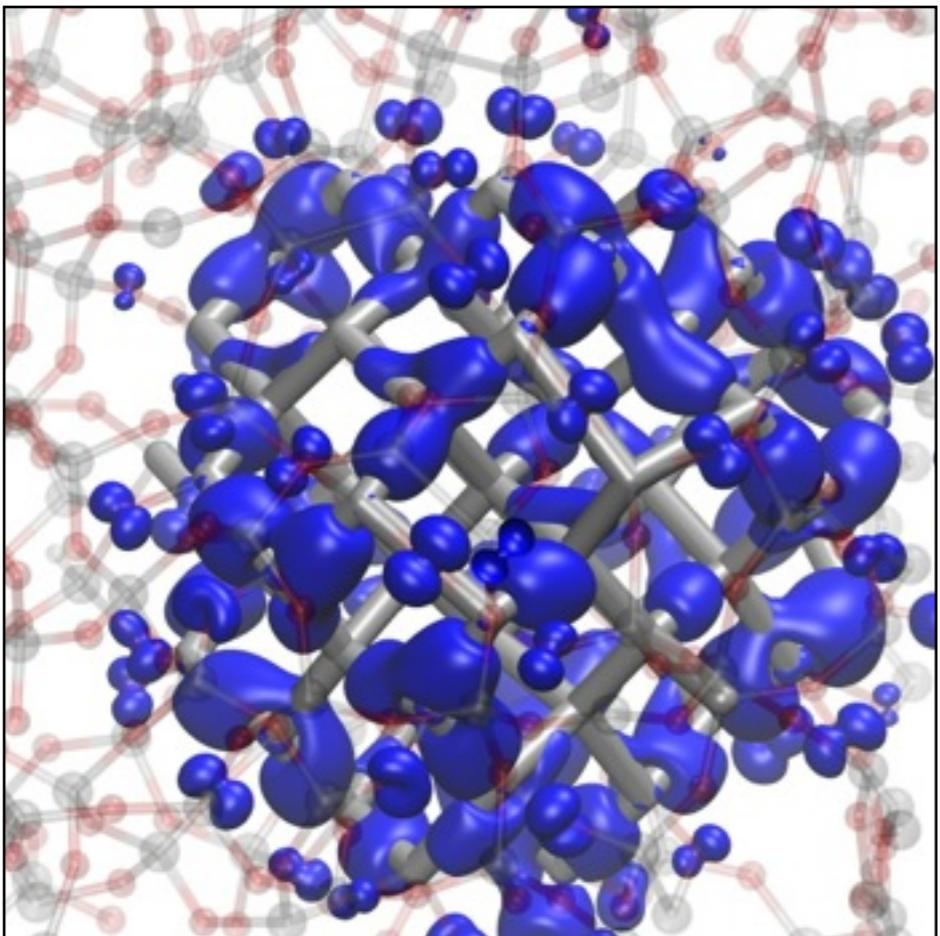


Si nanoparticles (NPs) in SiO₂: type I junction

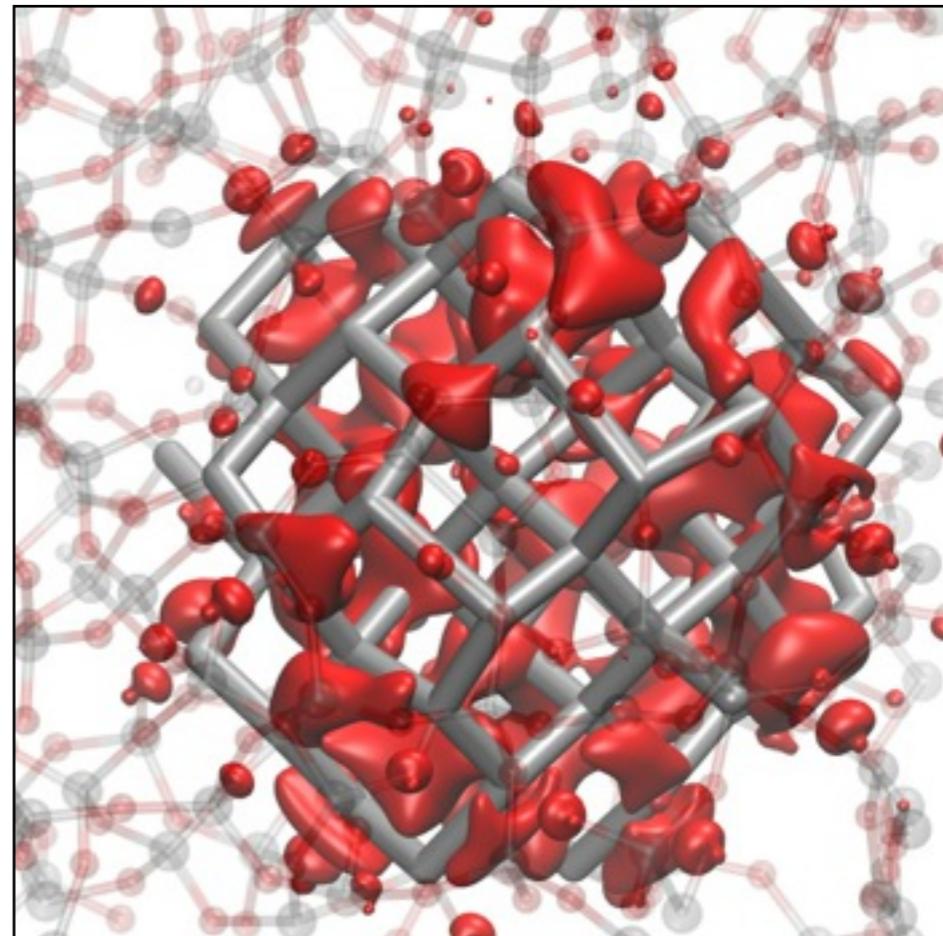
- Si NPs embedded in SiO₂ form a type I junction with their silica host
- Valence and conduction band edges localized inside Si NP => no charge transport
- NP LUMO may be pushed above SiO₂ CBM by compressive strain [T. Li, F. Gygi, G. Galli, PRL 2011]



valence band edge



conduction band edge

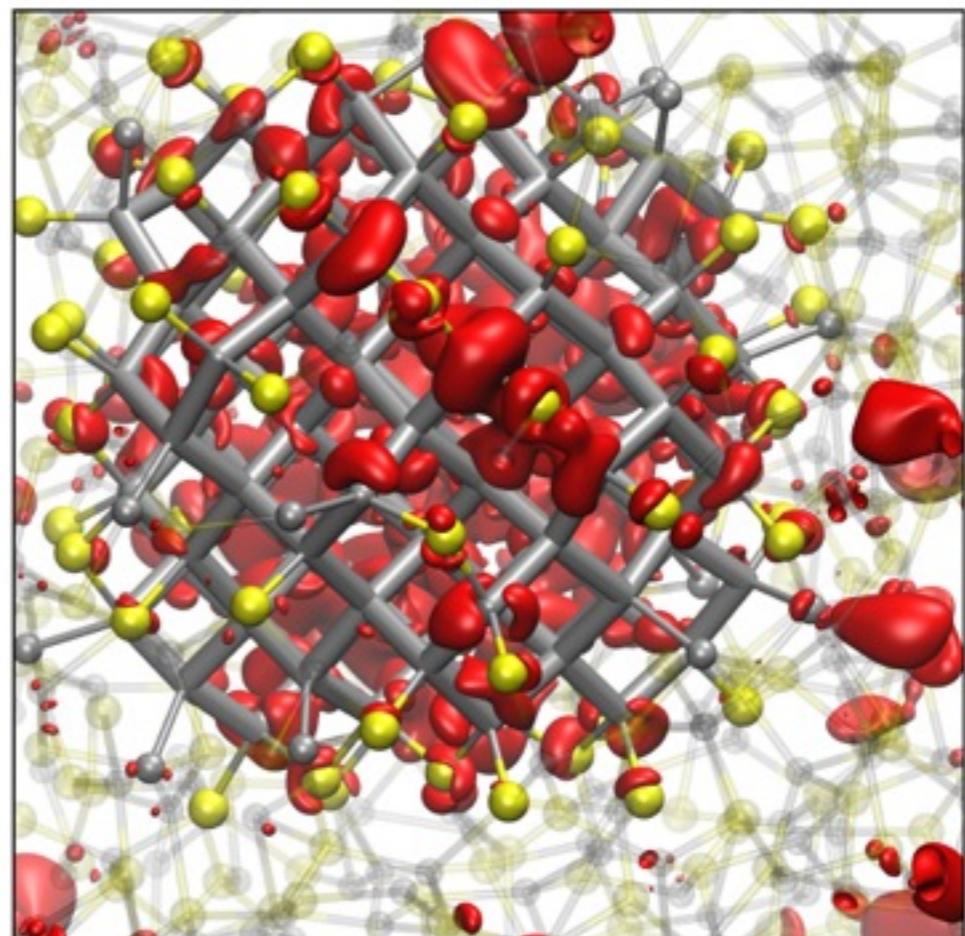
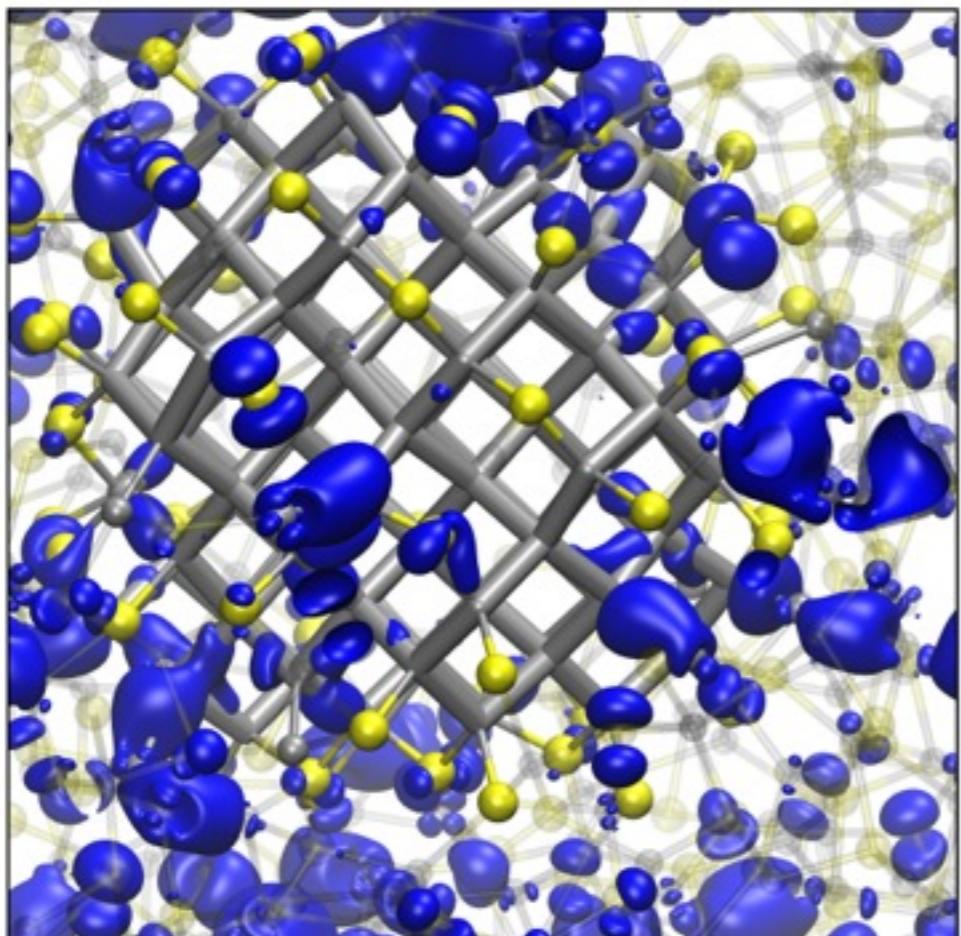
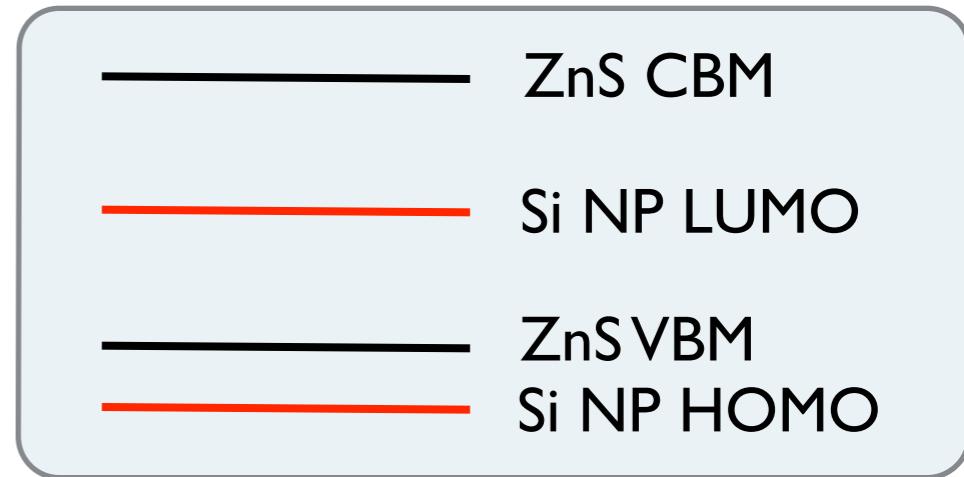


Si nanoparticles (NPs) in ZnS: *type II junction*

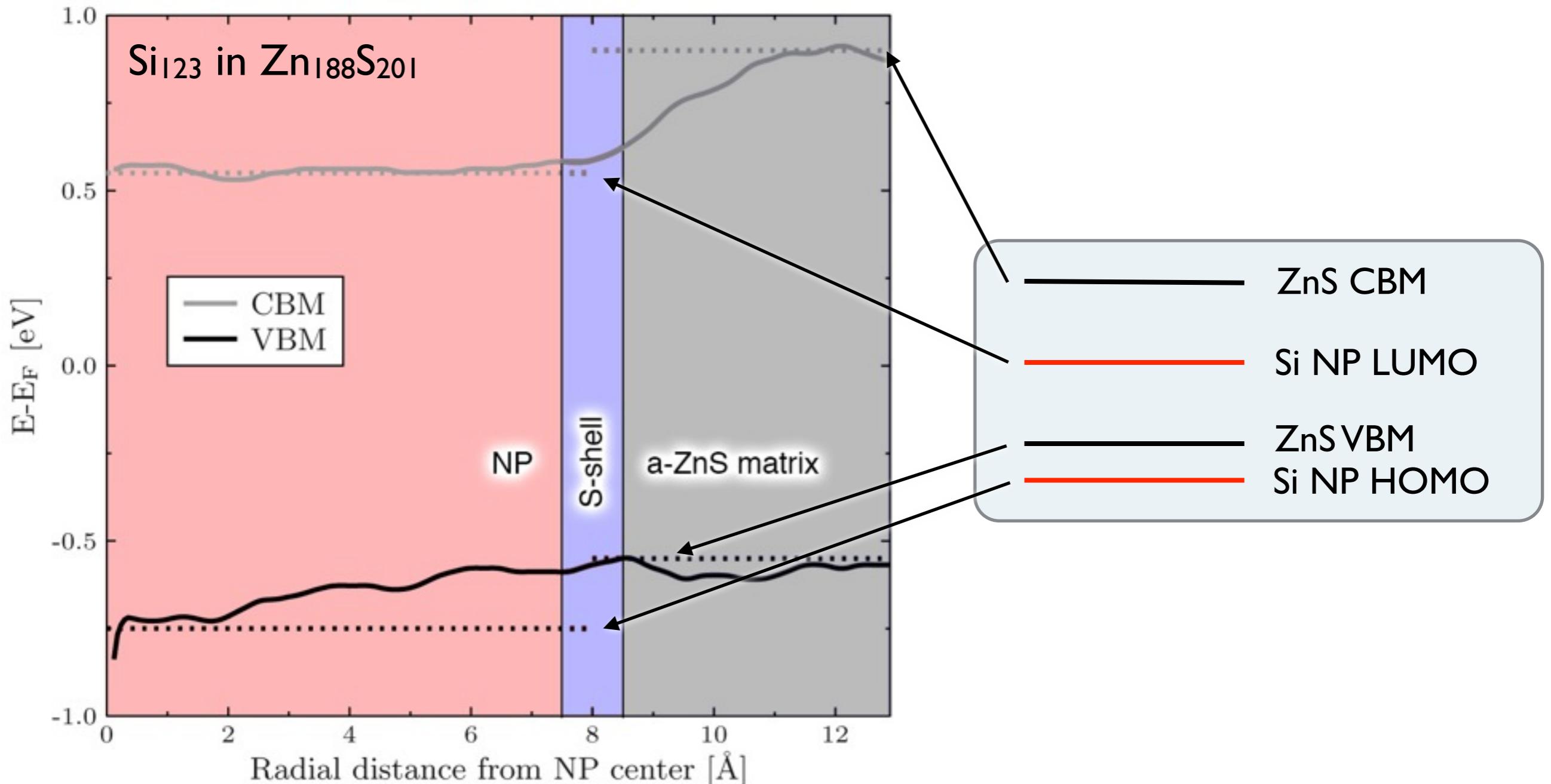
- Si NPs in ZnS form a type II junction at equilibrium density

- Charge-separated transport channels for electrons and holes may facilitate charge extraction and suppress recombination

- Hole transport through host matrix, highly desirable for solar cells

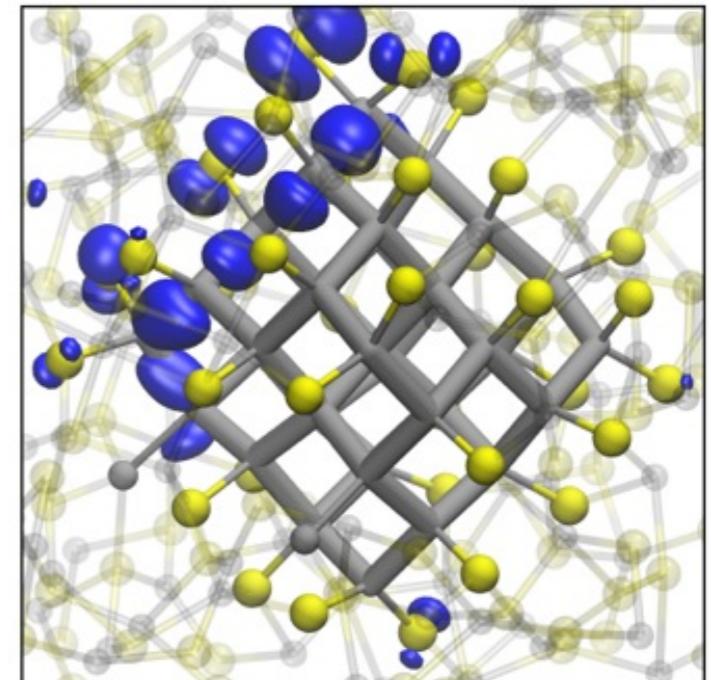


Si nanoparticles in ZnS: band alignment



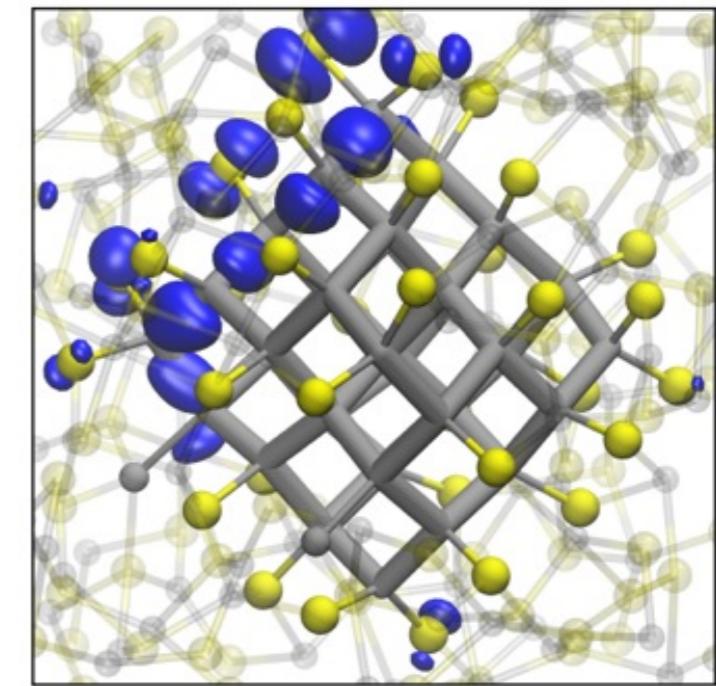
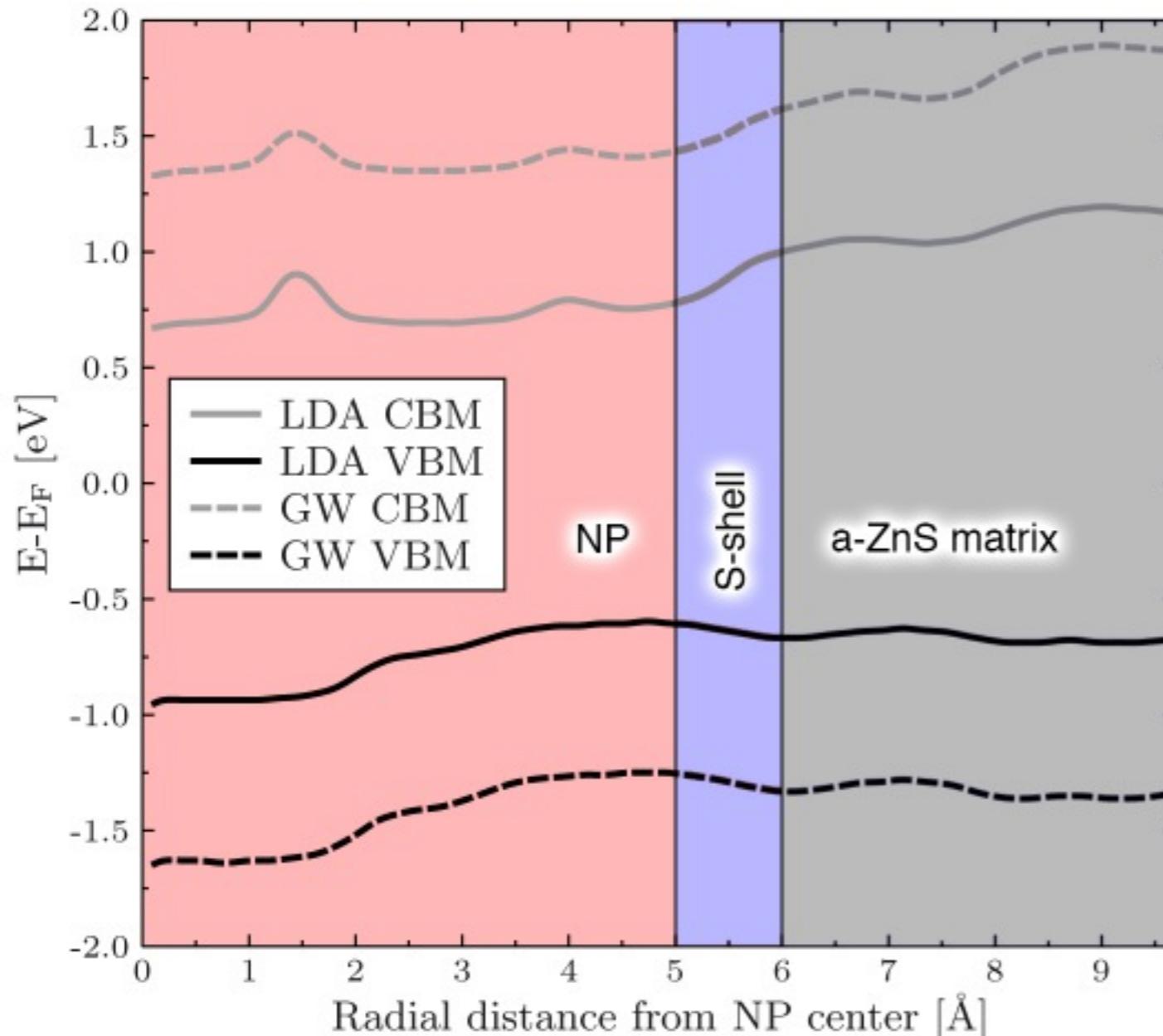
- Calculate band edge energies as a function of the radial distance from the center of the NP
- Formation of type II interface between Si NP and a-ZnS matrix, if, and only if, sulfur content is above a certain threshold

Band alignment from many body perturbation theory (GW)



- ➊ DFT-LDA band offsets reliable?
- ➋ Calculate band offsets from GW
- ➌ **New algorithmic developments allow GW calculations for a system as large as $\text{Si}_{35}\text{Zn}_{81}\text{S}_{100}$**

Band alignment from many body perturbation theory (GW)



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- ➌ **New algorithmic developments allow GW calculations for a system as large as $\text{Si}_{35}\text{Zn}_{81}\text{S}_{100}$**

➊ Many body corrections in GW approximation introduce mainly a rigid shift
➋ => confirms type II alignment

Summary

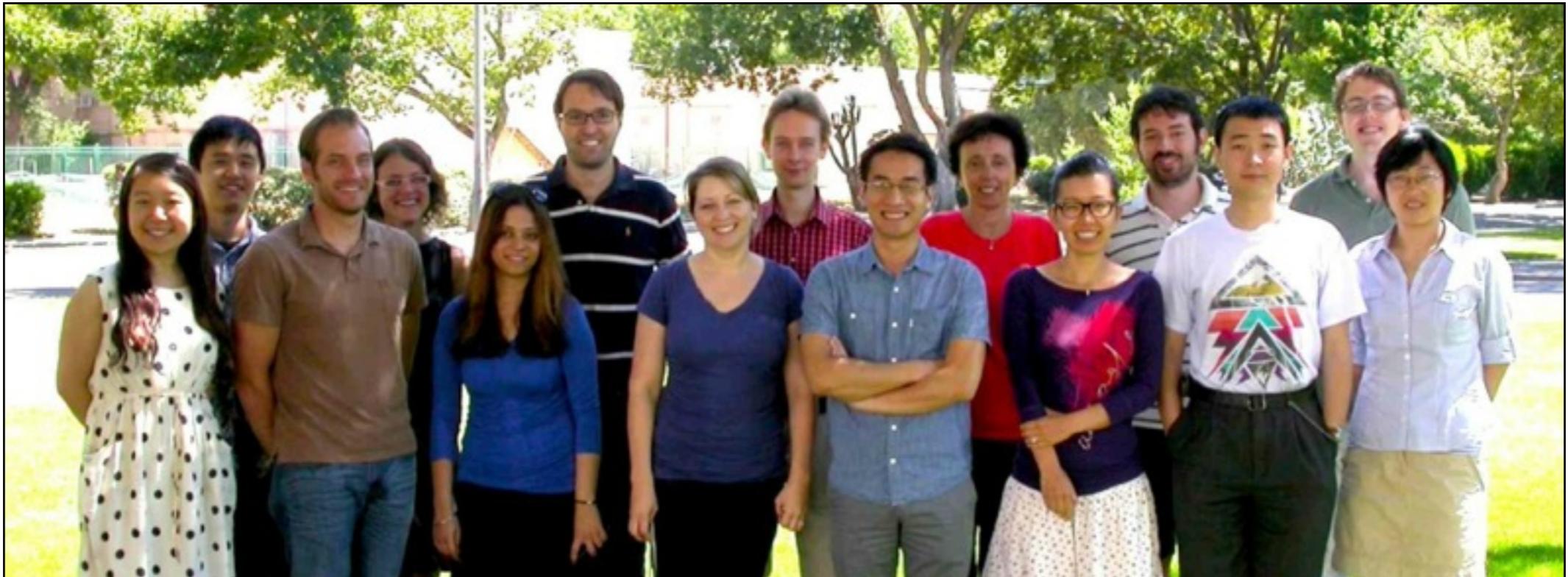
- Si and Ge nanocrystals with BC8 and ST12 core structures feature enhanced multiple exciton generation rates and lower electronic gaps, compared to diamond-like nanocrystals of the same size
- Ge ST12 wins on both relative and absolute energy scales, can be synthesized in colloidal solution

M.Vörös, S.Wippermann, B. Somogyi, A. Gali, D. Rocca, G. Galli, G. Zimanyi (under review)
S.Wippermann, M.Vörös, D. Rocca, A. Gali, G. Zimanyi, G. Galli, Phys. Rev. Lett. **110**, 046804 (2013)

- ZnS-embedded Si nanocrystals form a type II junction with the ZnS host in sulfur-rich conditions
- Band edges localized in different portions of nanocomposite => charge-separated transport channels for electrons and holes

S.Wippermann, M.Vörös, A. Gali, F. Gygi, G. Zimanyi, G. Galli, Phys. Rev. Lett. (in print)

Acknowledgements



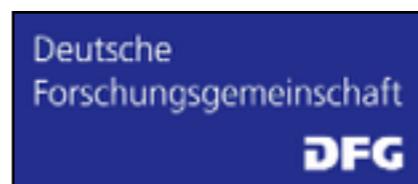
Thank you to my collaborators, the Giulia Galli,
Francois Gygi, Gergely Zimanyi and Adam Gali groups!



NSF/Solar DMR-1035468



NISE-project 35687



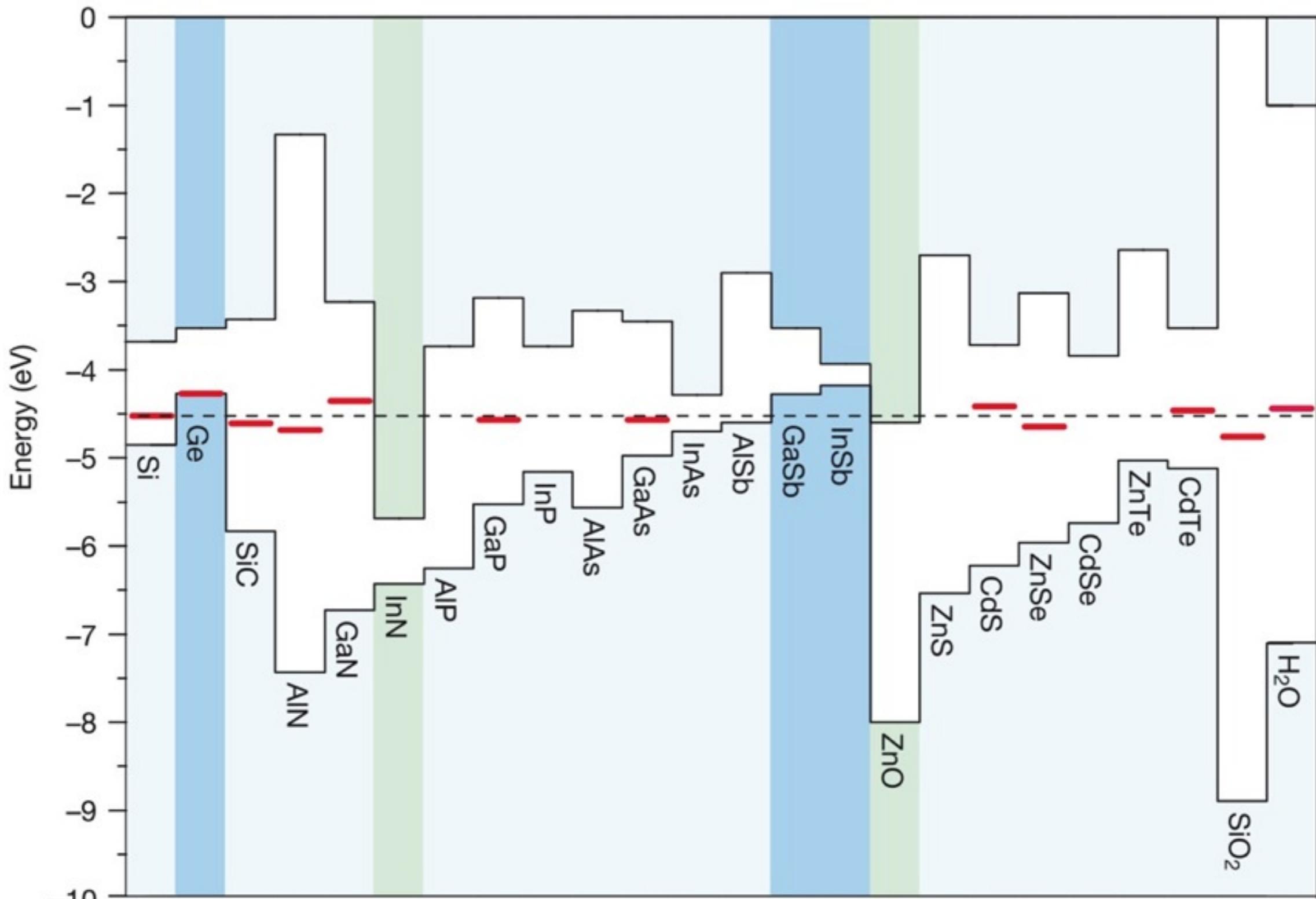
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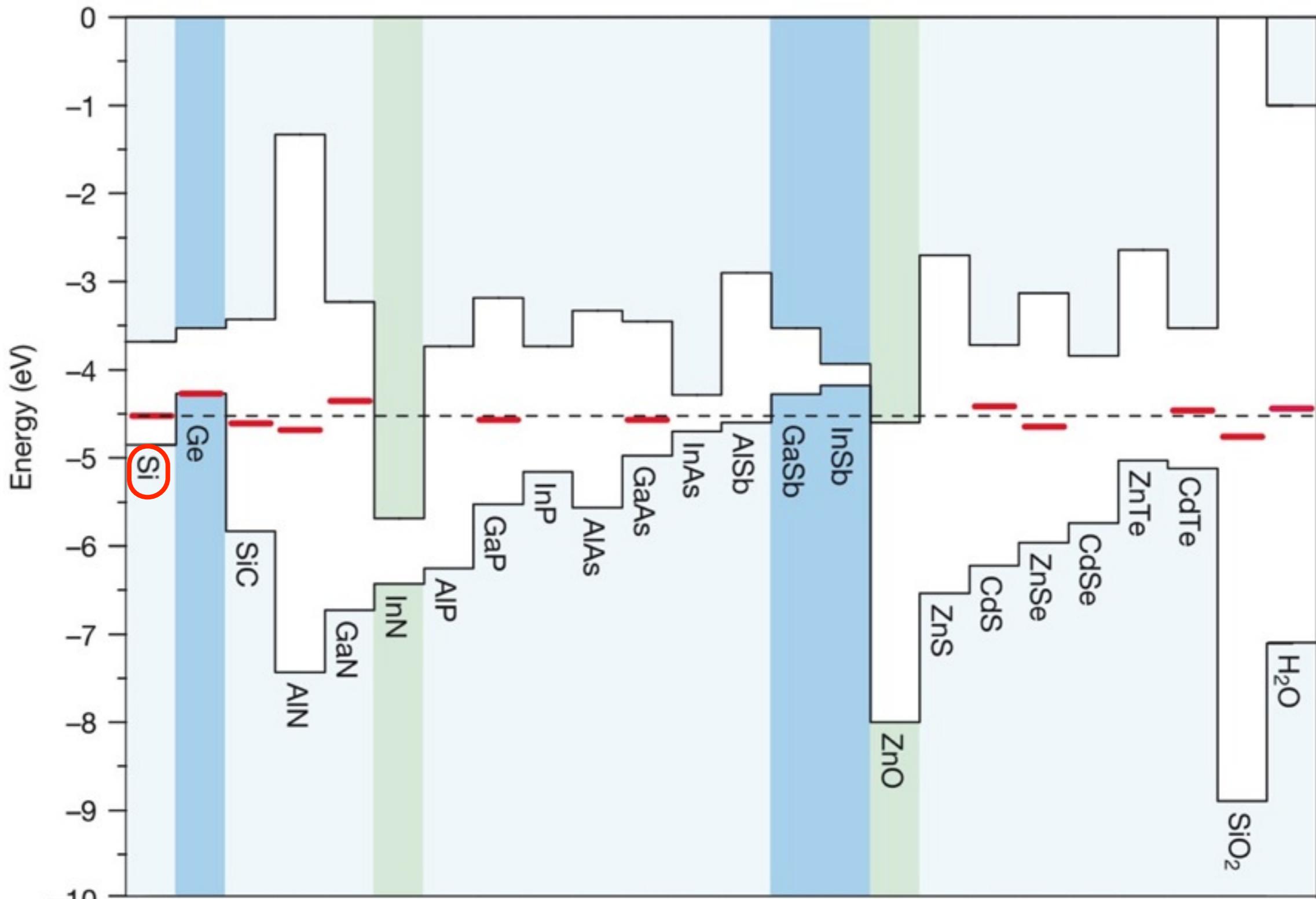
Bundesministerium
für Bildung
und Forschung

NanoMatFutur I3N12972

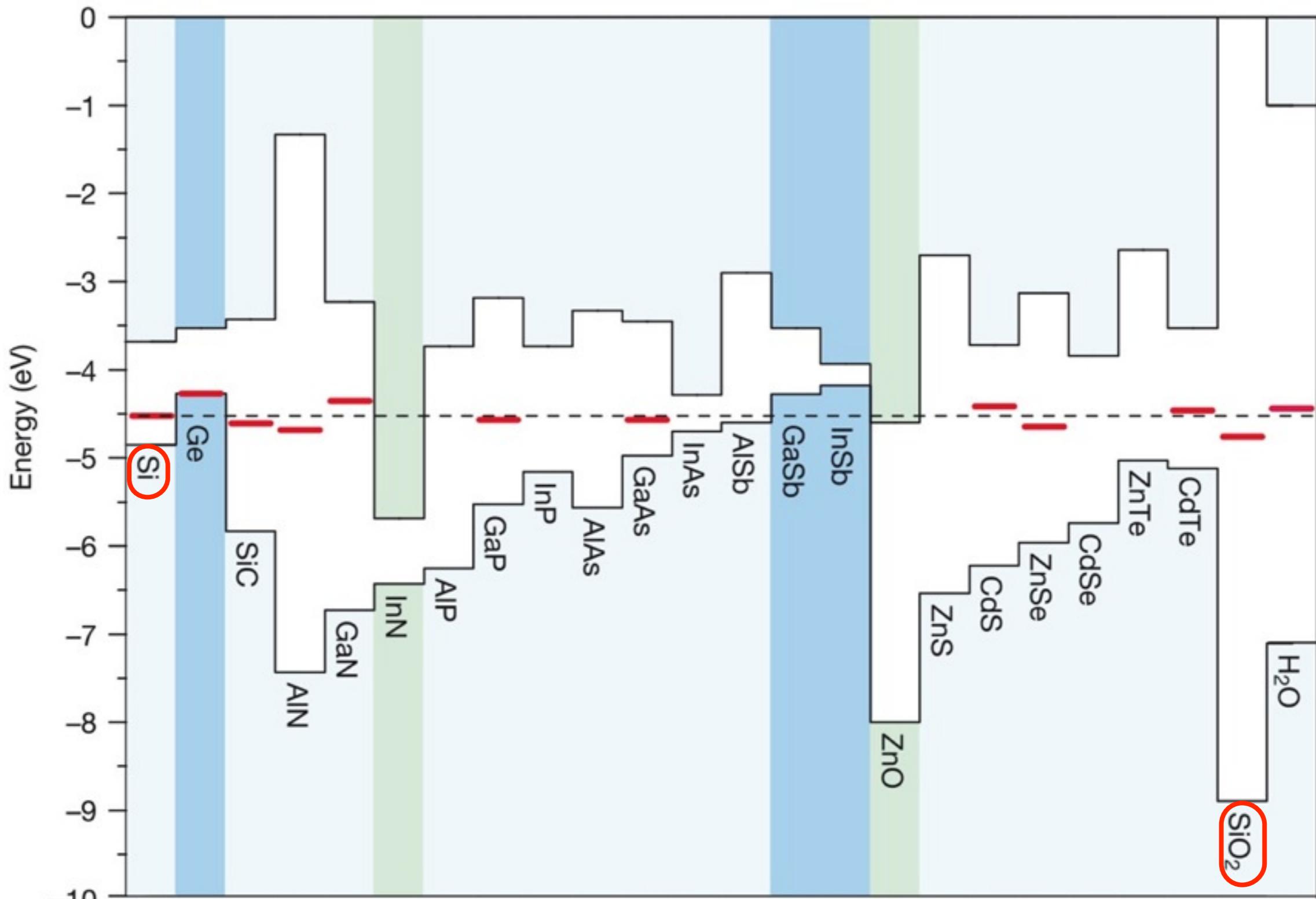
Band alignments of semiconductors



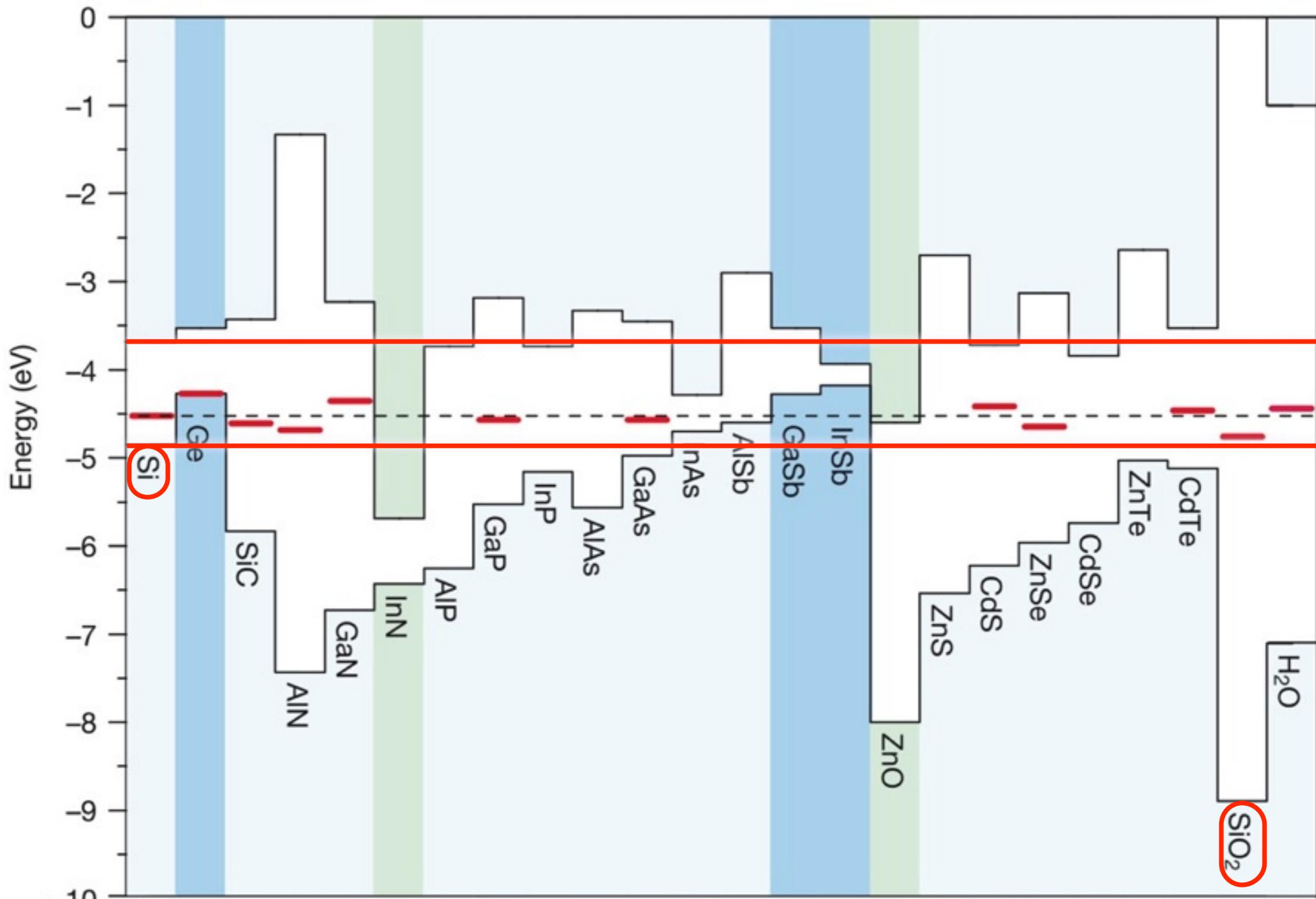
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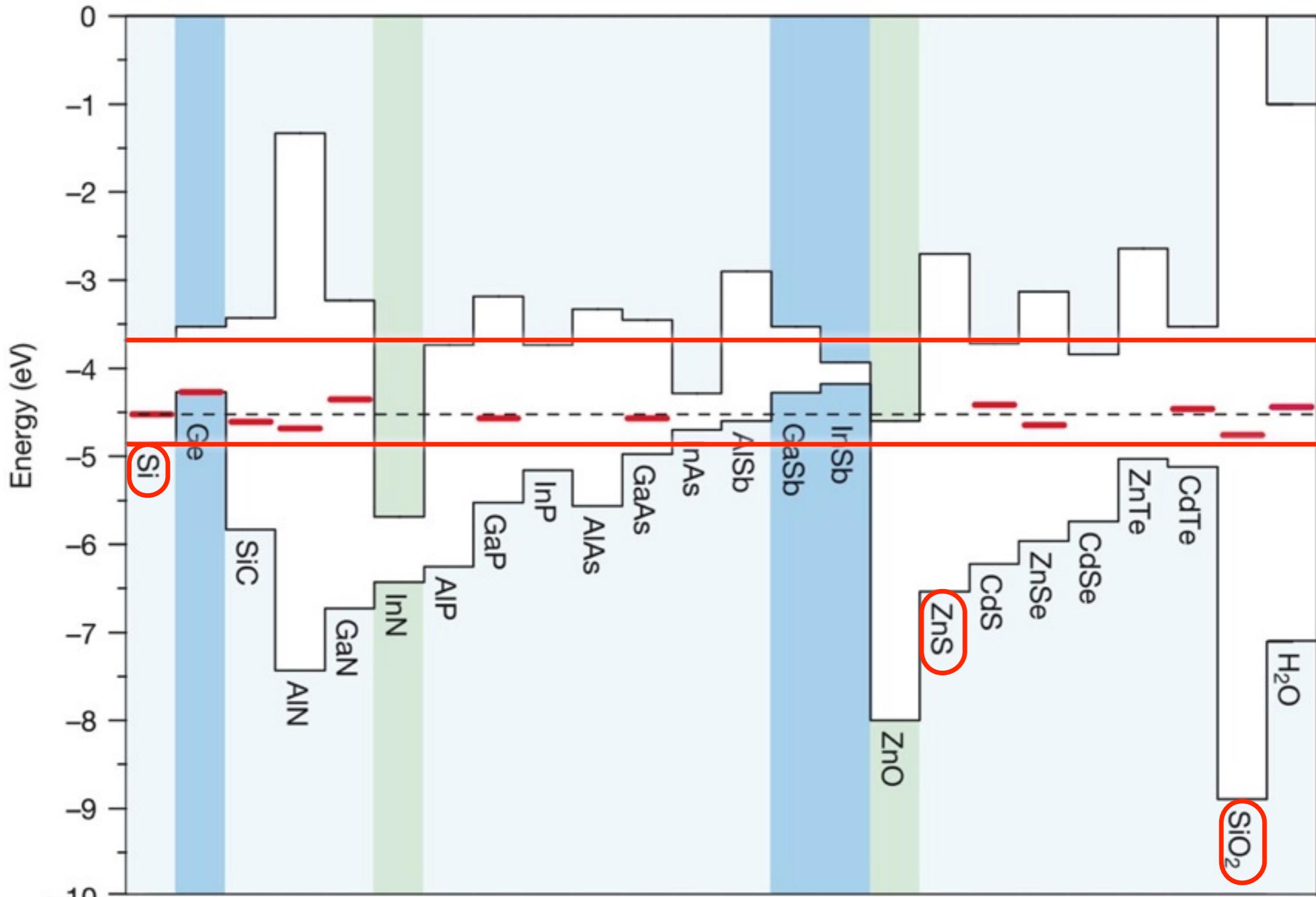
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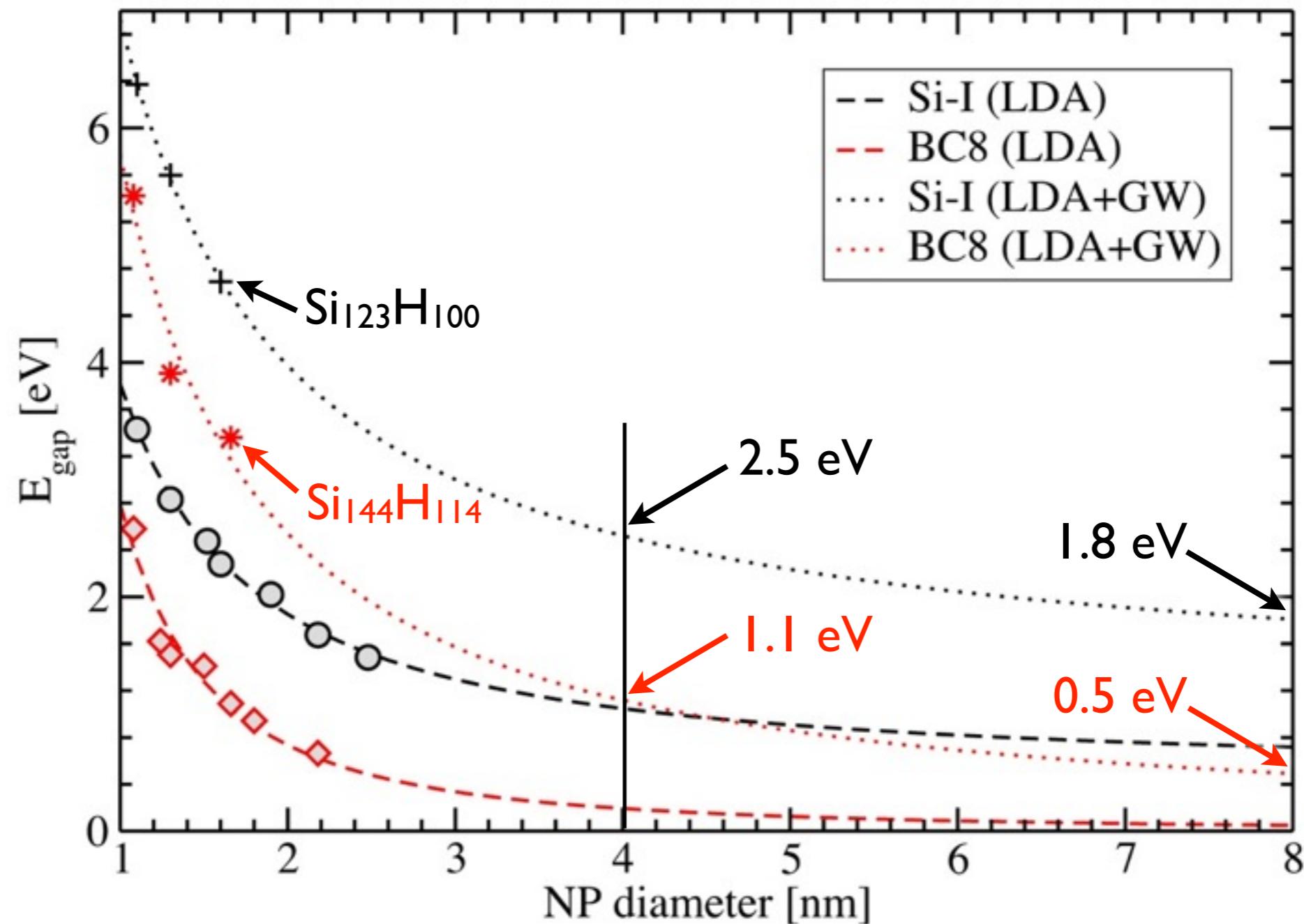
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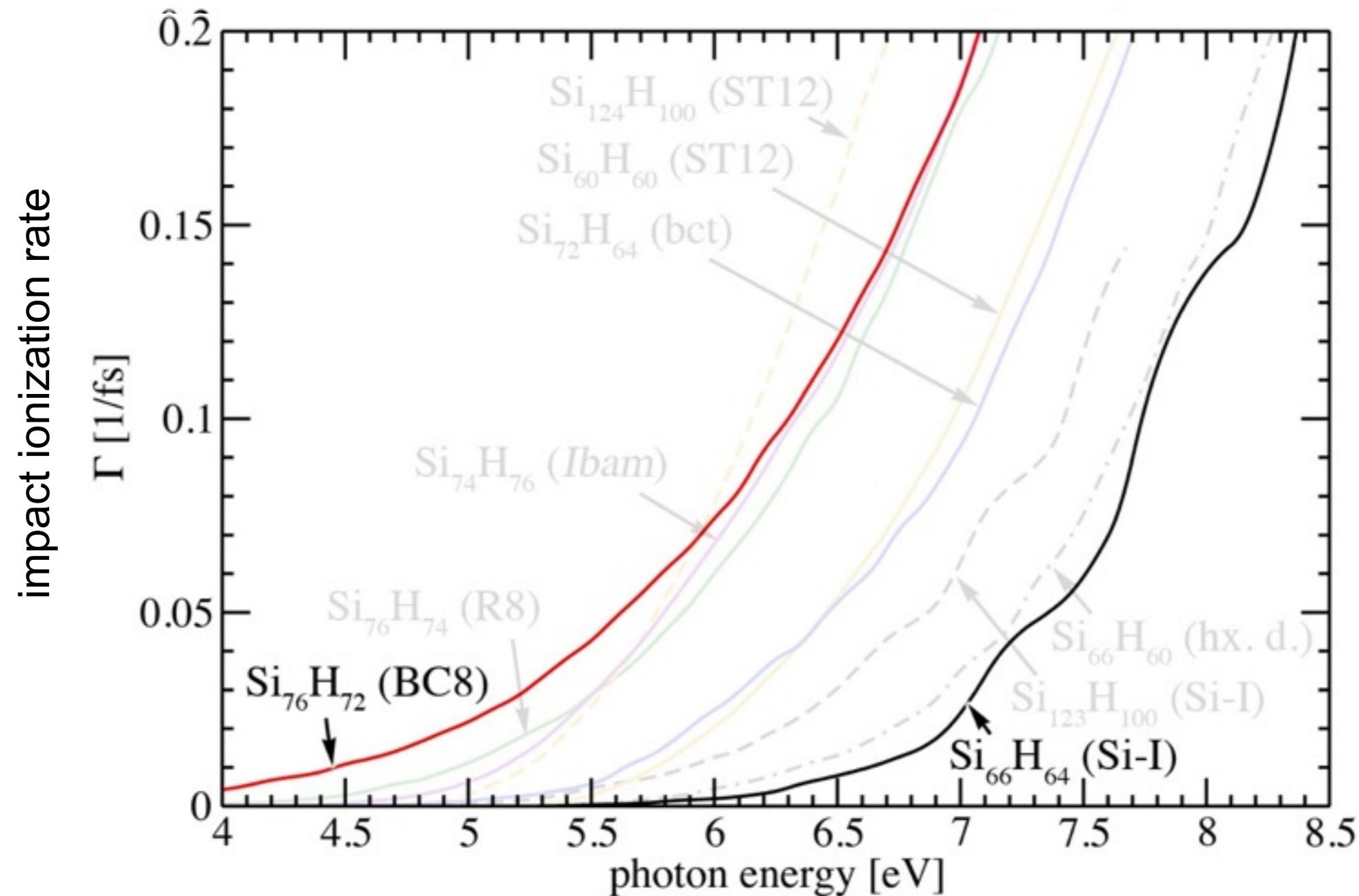
Band alignments of semiconductors



Band gaps of Si nanocrystals in LDA and GW



Strong gain for Si BC8 on absolute scale



- Impact ionization (II) is dominating contribution to MEG [5]; calculate II rates *ab initio*
- BC8 NPs feature lower activation threshold on absolute energy scale & order of magnitude higher impact ionization rate at same energies and same NP size!**

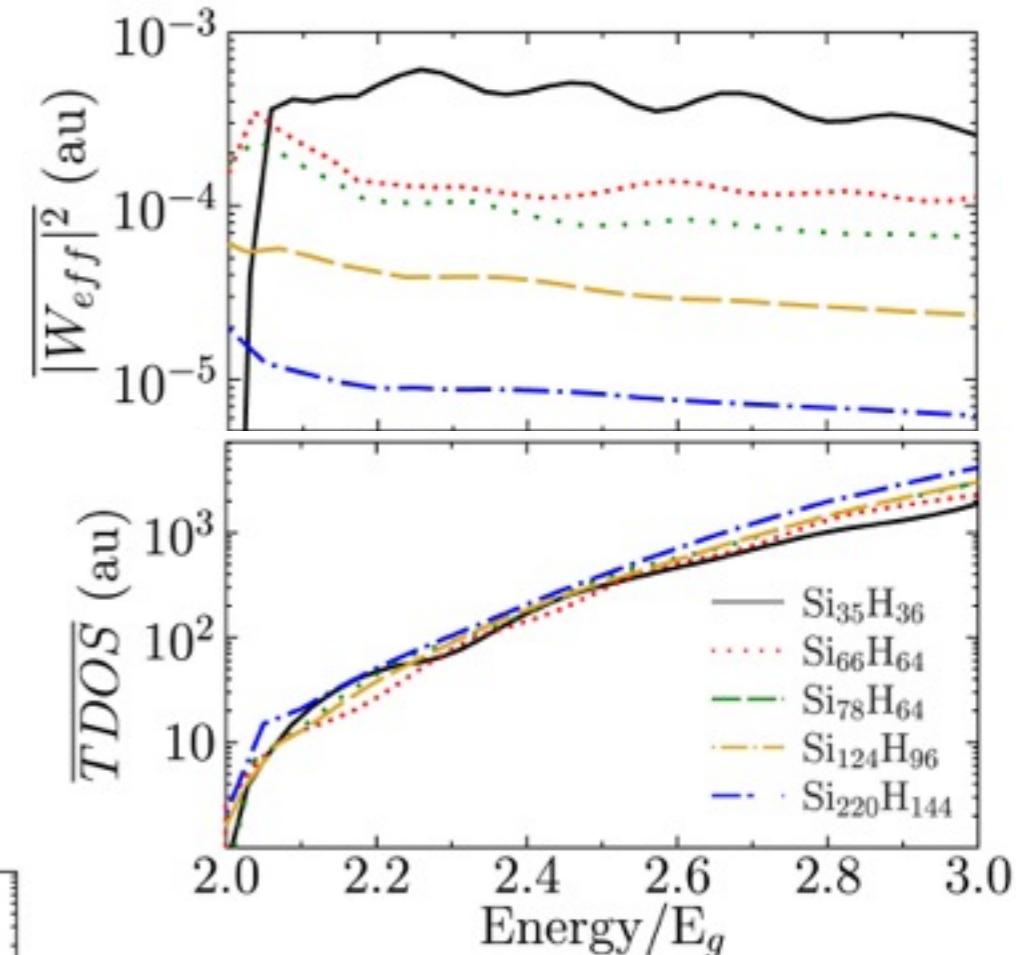
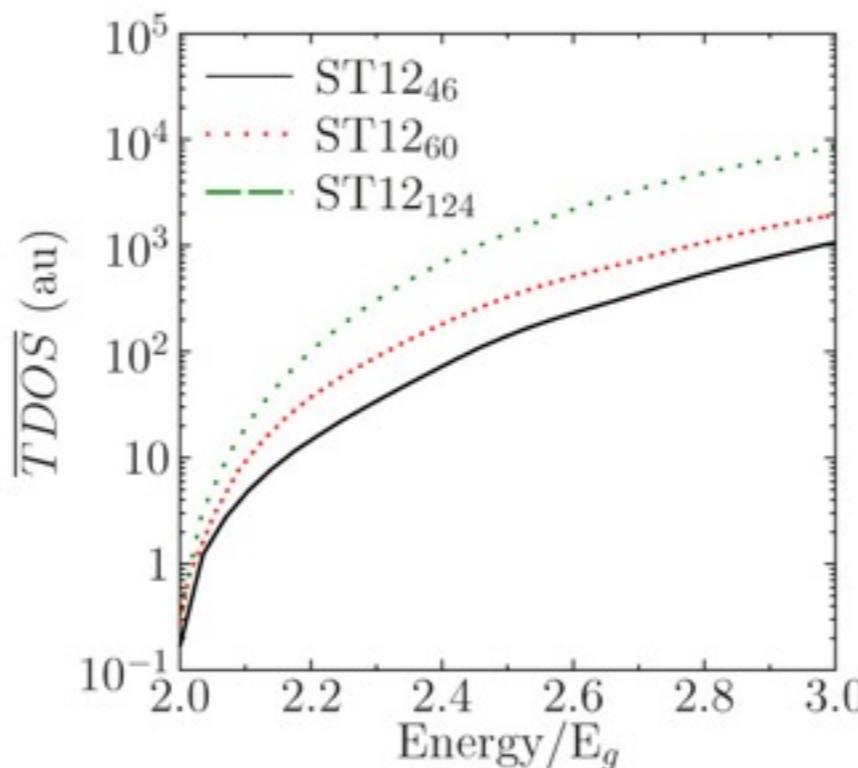
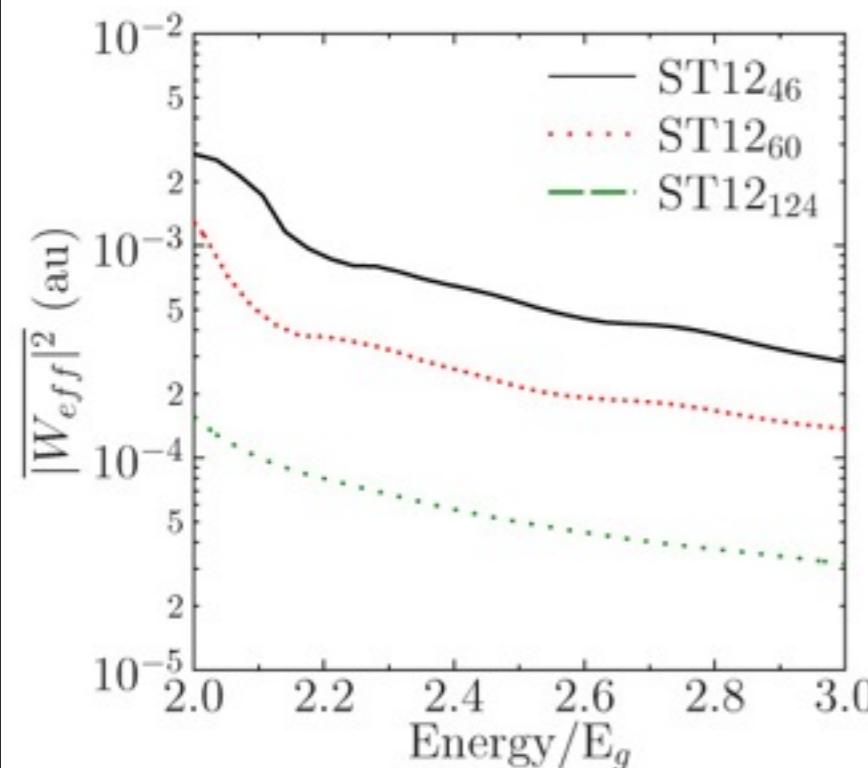
Ge: cubic diamond vs. ST12

$$\begin{aligned}\Gamma_i^{II} &= \frac{2\pi}{\hbar} \sum_f |\langle X_i | W | XX_f \rangle|^2 \delta(E_i - E_f) \\ &= \frac{2\pi}{\hbar} |W_{eff}^i|^2 \cdot TDOS_i\end{aligned}$$



cubic diamond: NP size increase reduces Coulomb interaction W_{eff} , trion DOS almost constant

=> impact ionization rate drops



ST12: W_{eff} reduced as for cubic diamond, **but TDOS increases**

=> impact ionization rate remains almost constant with increasing size