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

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**Multiple Exciton Generation (MEG)**

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

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

[A. Nozik, Physica E 14, 115 (2002)]
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**Key problems**

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

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Allotropes of Si and Ge

$c_{\text{cubic diamond}}$, semiconductor

$X_{35}H_{36}$

($X=\text{Si, Ge}$)
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- Cubic diamond, semiconductor
- BC8, semimetal
- $X_{34}H_{38}$
- $X_{35}H_{36}$ ($X=\text{Si, Ge}$)

[S. Ganguly et al., J. Am. Chem. Soc. 136, 1296 (2014)]
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Allotropes of Si and Ge

- **cubic diamond**, semiconductor
- **BC8**, semimetal
- **ST12**

S. Wippermann, M. Vörös, D. Rocca, A. Gali, G. Zimanyi, G. Galli,


[S. J. Kim et al., J. Mater. Chem. **20**, 331 (2010)]
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.
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

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 ST12 nanocrystals can be synthesized in solution.

M. Vörös, S. Wippermann, B. Somogyi, A. Gali, D. Rocca, G. Galli, G. Zimanyi (under review)
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Si nanocrystals embedded in a-ZnS

Create structural models for a-ZnS embedded \( \text{Si}_{35}, \text{Si}_{66}, \text{Si}_{123}, \text{Si}_{172} \) nanoparticles (NPs) from \textit{ab initio} molecular dynamics (MD)
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Pronounced gap reduction of embedded NPs due to sulfur shell formation
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- Create structural models for a-ZnS embedded \( \text{Si}_{35}, \text{Si}_{66}, \text{Si}_{123}, \text{Si}_{172} \) nanoparticles (NPs) from \textit{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 nanoparticles (NPs) in SiO$_2$: *type I junction*

- Si NPs embedded in SiO$_2$ 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 SiO$_2$ CBM by compressive strain [T. Li, F. Gygi, G. Galli, PRL 2011]
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

valence band edge

conduction band edge
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)

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

Band alignment from many body perturbation theory (GW)

DFT-LDA band offsets reliable?

Calculate band offsets from GW

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

Many body corrections in GW approximation introduce mainly a rigid shift

=> confirms type II alignment

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.

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.
Thank you to my collaborators, the Giulia Galli, Francois Gygi, Gergely Zimanyi and Adam Gali groups!
Band alignments of semiconductors

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Band gaps of Si nanocrystals in LDA and GW

- Si-I (LDA)
- BC8 (LDA)
- Si-I (LDA+GW)
- BC8 (LDA+GW)

Band gaps:
- 2.5 eV
- 1.8 eV
- 1.1 eV
- 0.5 eV

Materials:
- \( \text{Si}_{123}\text{H}_{100} \)
- \( \text{Si}_{144}\text{H}_{114} \)
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

\[
\Gamma^{II}_i = \frac{2\pi}{\hbar} \sum_f |\langle X_i | W | XX_f \rangle|^2 \delta(E_i - E_f) \\
= \frac{2\pi}{\hbar} |W_{eff}^i|^2 \cdot TDOS_i
\]

**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