Semiconducting nanoparticle solids for multi exciton solar cells: insights from \textit{ab initio} calculations

S. Wippermann*, M. Vörös, E. Scalise, A. Gali, G. Zimanyi, F. Gygi, G. Galli

*Max-Planck-Institut für Eisenforschung
Present group topics

surfaces/interfaces (2D)

- H$_2$O thin films on metal(-oxide) surfaces
- vibrational spectroscopy at solid-liquid interfaces

Lei Yang, Ulrich Biedermann

nanowires (1D)

- hybrid organic/inorganic nanowire solar cells
- atomic scale surface-supported nanowires

Taufik Adi Nugraha

quantum dots (0D)

- nanocrystal solids for multi-exciton solar cells

Emilio Scalise, Marton Vörös
Multi-Exciton Generation (MEG)

- Photons with $\hbar \nu > 2E_{\text{gap}}$ may create hot excitons that relax by creating additional excitons.
- Quantum confinement enhanced Coulomb interaction in nanoparticles (NPs) may increase MEG rates, compared to bulk semiconductors.
- Joint experiment-theory collaboration UC Davis and UC Santa Cruz, S. Kauzlarich (NP synthesis), S. Carter (devices and meas.), G. Galli and G. Zimanyi (theory).
MEG in real devices

O. Semonin et al., Science 334, 1530 (2011)

G. Zhai et al., Nanotechnology 23, 405401 (2012)
Need to improve transport => „infilling the vacuum“

- charge carrier diffusion length in NP-ligand films too short
- create NP-solids by embedding NPs in charge transport matrix
- impact of matrix on MEG?
Band alignments of semiconductors

Embedding Si nanoparticles in a-ZnS

Replace spherical region in 4x4x4 ZnS unit cell by Si (d = 1.1, 1.3, 1.6, 1.9 nm) & amorphize matrix by first principles molecular dynamics

DFT-LDA (QBox), $E_C = 80\text{Ry}$, $\tau = 2\text{fs}$, $T=2400\text{K}$, Si-atoms free to move for $T<750\text{K}$

=> MD estimated to take $>10\text{ Mio. CPU h}$, whole group had „only“ 2 Mio. CPU h per year!

Let’s write a grant application for computer time, take a little detour and come back later
Dilemma: *confinement vs. gap size*

Quantum confinement in NPs:
- Enhances Coulomb interaction
- Enlarges electronic gap
  => MEG threshold beyond solar spectrum

„Although Si has low [...] critical energy and large [...] figure of merit, its absorption spectrum for small NP sizes does not match the solar spectrum“

[A. Zunger *et al.*, Nano Lett. **8**, 3174 (2008)]
Silicon allotropes (under pressure)

Silicon allotropes (under pressure)

β-tin (Si-II)

pressure (~12 GPa)

E_g = 1.1 eV

metal

slow pressure release (~8 GPa)

R8 (Si-XII)

ambient pressure

E_g = 0.24 eV

BC8 (Si-III)

annealing (470 K)

hex. diam. (Si-IV)

E_g = 0.95 eV

Si-I
Silicon allotropes (under pressure)

- **β-tin (Si-II)**: Metal
  - Pressure (~12 GPa)
  - Slow pressure release (~8 GPa)

- **Si-XIII, Si-IX**: Only incomplete structural information known
  - Fast pressure release (<100ms)

- **R8 (Si-XII)**: 
  - Ambient pressure
  - $E_g = 0.24$ eV

- **BC8 (Si-III)**: Semimetal
  - Annealing (470 K)

- **Si-I**: 
  - Hex. diam. (Si-IV)
  - $E_g = 0.95$ eV

- **Eg = 1.1 eV**
Silicon allotropes (under pressure)

- Si-I
- β-tin (Si-II)
- pressure (~12 GPa)
- metal
- fast pressure release (<100ms)

- Si-III, Si-IX
- only incomplete structural information known
- slow pressure release (~8 GPa)

- Si-XIII, Si-IX
- fast pressure release (<100ms)

- R8 (Si-XII)
- ambient pressure
- E_g = 0.24 eV

- BC8 (Si-III)
- semimetal
- annealing (470 K)

- E_g = 1.1 eV

- (yet) hypothetical phases of Si

- hex. diam. (Si-IV)
- E_g = 0.95 eV

- Ibam (Si-IX??)
- bct
- ST12
Silicon NPs with allotrope cores

Si$_{34}$H$_{36}$ (R8)

Si$_{34}$H$_{38}$ (BC8)

Si$_{42}$H$_{48}$ (Ibam)

Si$_{35}$H$_{36}$ (cd)

Si$_{39}$H$_{40}$ (hd)

Si$_{46}$H$_{52}$ (ST12)

Si$_{44}$H$_{48}$ (bct)
Surface reconstructions

$\text{Si}_{102}\text{H}_{80}$ (BC8)

$E_g = 1.41 \text{ eV}$
Surface reconstructions

$\text{Si}_{102}\text{H}_{68}$ (BC8)

$E_g = 1.47$ eV
Surface reconstructions

$\text{Si}_{102}\text{H}_{56}$ (BC8)

$E_g = 1.01 \text{ eV}$
Electronic gaps (DFT-LDA)

BC8 is a semi-metal in the bulk, 0.3 eV direct overlap at the H-point.
Quantum confinement opens gap in BC8 nanoparticles.
BC8 NPs feature much smaller gaps than Si-I NPs.
BC8 is a semi-metal in the bulk, 0.3 eV direct overlap at the H-point

Quantum confinement opens gap in BC8 nanoparticles

BC8 NPs feature much smaller gaps than Si-I NPs
GW calculations confirm trends observed at single particle level of theory*

**Si-BC8 NP GW gaps ideal for solar energy conversion in 4-8nm size range, where MEG is still efficient for Si-I NPs**

GW gaps provide upper estimate: reconstructions, excitonic effects further reduce gaps

*Fitting performed including known GW bulk gaps; theory: H.-V. Nguyen et al., PRB 85, 081101 (2012)

[M. Hanna et al., J. Appl. Phys. 100, 074510 (2006)]
Impact ionization (II) is dominating contribution to MEG*; calculate II rates from *ab initio* [M. Vörös et al., PRB 87, 155402 (2013)]

**BC8 NPs** feature lower activation threshold on absolute energy scale & order of magnitude higher impact ionization rate at same energies and same NP size!

Impact ionization (II) is dominating contribution to MEG*; calculate II rates from \textit{ab initio} [M. Vörös \textit{et al.}, PRB 87, 155402 (2013)]

BC8 NPs feature lower activation threshold on absolute energy scale & order of magnitude higher impact ionization rate at same energies and same NP size!

"detour" summary

predict both Si BC8 and Ge ST12 NPs to feature enhanced MEG rates compared to diamond-like NPs
predict both Si BC8 and Ge ST12 NPs to feature enhanced MEG rates compared to diamond-like NPs

High-Pressure Core Structures of Si Nanoparticles for Solar Energy Conversion

S. Wippermann, ¹,² M. Vörös, ³ D. Rocca, ¹ A. Gali, ³ ⁴ G. Zimanyi, ² and G. Galli ¹,²

¹Department of Chemistry, University of California, Davis, California 95616, USA
²Department of Physics, University of California, Davis, California 95616, USA
³Department of Atomic Physics, Budapest University of Technology and Economics, Budafoki út 8, H-1111 Budapest, Hungary
⁴Institute for Solid State Physics and Optics, Wigner Research Center for Physics, Hungarian Academy of Sciences,
P.O. Box 49, H-1525 Budapest, Hungary

(Received 1 August 2012; published 24 January 2013)

Germanium nanoparticles with non-diamond core structures for solar energy conversion

Márton Vörös, ⁴,a Stefan Wippermann, ⁵ Bálint Somogyi, ⁴ Adam Gali, ⁶,d Dario Rocca, ⁶,d Giulia Galli ⁷,a and Gergely T. Zimanyi ⁷,a

Si BC8 and Ge ST12 NPs can now be synthesized colloidally, but no MEG measurements (yet)
obtained the 10 Mio. CPU h necessary to 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} 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 nanocrystals (NCs) in SiO$_2$: type I junction

- Si NCs embedded in SiO$_2$ form a type I junction with their silica host.
- Valence and conduction band edge states localized inside Si NC => no charge transport.
- NC LUMO may be pushed above SiO$_2$ CBM by compressive strain [T. Li, F. Gygi, G. Galli, PRL 2011].
Si nanocrystals (NCs) in ZnS: *type II junction*

- Si NCs 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 nanocrystals in ZnS: *band alignment*

Calculate band edge energies as a function of the radial distance from the center of the nanocrystal.

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 $\text{Si}_{35}\text{Zn}_{81}\text{S}_{100}$

Band alignment from many-body perturbation theory (GW)

- Many body corrections in GW approximation introduce mainly a rigid shift
  
  \[ \Rightarrow \text{confirms type II alignment} \]

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

Where do we go from here?

- **impact of embedding on MEG?** => embedded systems prohibitively large for our present impact ionization (II) code
- recent algorithmic advances in calculating dielectric tensor expected to enable MEG rate calculation
- **need to work on the II code**

- NSF grant funding joint experiment-theory collaboration ended in 2014
- embedding by ALD rather expensive anyway
- **fully colloidal approach to both NP synthesis and embedding** seems very promising
- even more complex systems, strong need to understand surface chemistry and impact on macroscopic properties
- **collaboration with Dmitri Talapin, choose InAs-NPs and Sn$_2$S$_6^{4-}$ ligands as model system**
Colloidal approach to synthesis and embedding

Traditional organic hydrocarbon ligands can be exchanged for metal chalcogenide complexes (MCCs), e.g. Sn$_2$S$_6^{4-}$.

MCCs can form conductive glue between NPs.

Gentle heat treatment transforms Sn$_2$S$_6^{4-}$ → SnS$_2$.

Interface structure largely unknown.

Sn$_2$S$_6^{4-}$ ligands assumed to adsorb intact as structural units on In-rich surface of InAs-NPs.

[D. Talapin et al., Science 324, 1417 (2009), JACS 134, 18585 (2012), Nature Mat. 12, 410 (2013)]
Possible structures realized at NP-matrix interface

Surprise: DFT predicts $\text{Sn}_2\text{S}_6^{4-}$ on bare In-rich InAs-surfaces highly unstable, dissociates without barrier.

- Surface reconstructions
- S passivation
- S subsurface substitution
- SnS or InS surface layer formation
- Adsorption of ligands on (combinations of) such surface structures
Calculating free energies: a grand canonical approach

free energy: \[ \Delta G = E_{tot} - E_{ref} - \sum_{i} n_i \mu_i \]

\[ \mu_{In} \leq \mu_{In}(\text{bulk}) \]
\[ \mu_{As} \leq \mu_{As}(\text{bulk}) \]
\[ \mu_{Sn} \leq \mu_{Sn}(\text{bulk}) \]
\[ \mu_{S} \leq \mu_{S}(\text{bulk}) \]
\[ \mu_{N} \leq \frac{1}{2} \mu_{N_2}(\text{gas}) \]
\[ \mu_{H} \leq \frac{1}{2} \mu_{H_2}(\text{gas}) \]

\[ \mu_{In} + \mu_{As} = \mu_{InAs} \]
\[ \mu_{Sn} + 2\mu_{S} = \mu_{SnS_2} \]
\[ 2\mu_{N} + 4\mu_{H} = \mu_{N_2H_4} \]

μ corresponds to free energy at which reservoir provides particles

plot phase diagram as function of \( \Delta \mu_{In}, \Delta \mu_{S}, \Delta \mu_{H} \)

=> relative thermodynamic stability of different structures at specific synthesis conditions
InAs(100)-Sn$_2$S$_6$ surface phase diagram ($\mu_{\text{In}}$)

- **S-rich & H-rich**
- **Sn @ InAs**
- **InAs surface reconstructions**
- **S + Sn$_2$S$_6$-ligand @ InAs**
InAs(100)–Sn$_2$S$_6$ surface phase diagram ($\mu_S$)
InAs(100)-Sn$_2$S$_6$ surface phase diagram ($\mu_S, \mu_{in}$)
Towards NP-superlattices

- complete phase diagrams for relevant surface orientations
- construct NP-ligand superlattices from identified minimum energy structures
- connect to experiment: Raman spectroscopy
Intermediate bands (IB)

- optimal band gap of 2.4 eV and an IB
- IB should be partially filled
- optical transitions should be bright
- finite width of IB may help reduce non-radiative recombination
- existing realizations: intra-gap impurity states in the bulk epitaxial quantum dots

Proposing to implement IB in colloidal nanoparticle solar cells

A. Martí et al., IEE Trans. 48, 2394 (2001)
Intra-gap state formation in CdSe NPs

- intra-gap state formation due to surface reconstruction
- persistent feature at size range accessible to us (DFT)
- $E_{\text{gap, bulk}} \sim 1.8 \text{ eV}$, confinement widens gap to 2-2.5 eV range in $d = 4 \text{ nm}$ CdSe NPs

Partial filling of intra-gap state

- photo-doping: IGS alone can support upconversion through 2-photon absorption
- chemical doping: $E_0$ (redox potential for a redox couple) > $E_{IGS}$ of NP

Transitions optically active?

- HOMO localized to one facet, LUMO and IGS on the other
- IGS $\rightarrow$ LUMO transitions significantly brighter than HOMO $\rightarrow$ IGS and HOMO $\rightarrow$ LUMO transitions

likely results in unfavourable steady state filling of intra-gap state
Intermediate band formation in NP-solids

- Intermediate band (IB) with finite width forms in simple cubic (SC) and face-centered cubic (FCC) Cd$_{15}$Se$_{15}$ solids.
- **Width of the IB** depends on NP separation, might be controlled by appropriately chosen ligands.

![Diagram showing energy bands for SC and FCC structures](image-url)
Intermediate band formation possible in core/shell-NPs?

CdSe NPs interesting from conceptual point of view, but low intensity HOMO → IGS transition, IGS due from surface reconstruction probably not very stable

core/shell systems more promising?

Klimov group reports high MEG yields in PbSe/CdSe core/shell-NPs

C. Cirlugano et al., Nat. Comm. 5, 4148 (2014)
Multi-exciton generation + intermediate bands?

(a) $E_{\text{abs}} > 2E_{\text{IC}}$
(b) $E_{\text{abs}} > E_{\text{VC}} + E_{\text{IC}}$
(c) $E_{\text{abs}} > 3E_{\text{IC}}$
(d) $E_{\text{abs}} > 2E_{\text{VI}}$
Summary

lower MEG threshold, e.g. in Si & Ge high pressure core NPs

embedding NPs in charge transport matrix, type II junction for Si-NP/ZnS

building realistic NP-matrix interface models from ab initio thermodynamics

dream: simultaneous utilization of low & high energy parts of solar spectrum by IB & MEG in single NP-system

looking for ways to form intermediate bands in colloidal NPs, e.g. surface reconstructions or core/shell

SW et al., PRL 110, 046804 (2013); M. Vörös, SW et al., J Mat Chem A 2, 9820 (2014)

SW et al., PRL 112, 106801 (2014)
Acknowledgements

Collaborating Groups

Theory:
Giulia Galli (U Chicago)
Francois Gygi (UC Davis)
Gergely Zimanyi (UC Davis)
Adam Gali (Budapest Univ.)

Experiment:
Dmitri Talapin (U Chicago)
Sue Kauzlarich (UC Davis)
Sue Carter (UC Santa Cruz)

Emilio Scalise
Taufik Adi Nugrah
Lei Yang
Ulrich Biedermann

NERSC
NISE-project 35687

DFG
Deutsche Forschungsgemeinschaft

Bundesministerium
für Bildung und Forschung

NanoMatFutur 13N12972

NSF/Solar DMR-1035468

Marton Vörös
Dario Rocca
**Density functional theory (DFT):**

**Hohenberg-Kohn theorem:**

\[
E[n] = T_0[n] + \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} dr\,dr' + \int n(r)V(r)\,dr + E_{XC}[n]
\]

[Walter Kohn, Nobel Prize for chemistry in 1998]

**Starting point:** initial geometry

- \[E_{XC}[n] \approx E_{XC}^{LDA}[n] = \int n(r)\epsilon_{XC}^{hom}(n(r))\,dr\]

- **atomic positions**

---

**Kohn-Sham self-consistent electron structure**

\[
\left\{-\frac{\nabla^2}{2} + \int \frac{n(r')}{|r - r'|} \, dr' + V(r) + \frac{\delta E_{XC}^{LDA}}{\delta n(r)} \right\} \psi_j(r) = \epsilon_j \psi_j(r)
\]

**Structurally relaxed ground-state**

\[
n(r) = \sum_{\text{occ.}} |\psi_j(r)|^2
\]

---

**vibrational and thermal properties**

**electronic properties**

**spectroscopic and transport properties**
Excited states (GW/BSE)

DFT disregards screened $e^-e^-$ interaction and $e^-h$ interaction for excited states $\Rightarrow$ band gap underestimation, wrong distribution of spectral weights

Perturbative approaches for including screening (GW) and $e^-h$ interaction (Bethe-Salpeter), starting from Quantum Liouville equation

\[
i \frac{d\hat{\rho}(t)}{dt} = \left[ \hat{\mathcal{H}}(t), \hat{\rho}(t) \right]
\]

\[
\rho(r, r', t) = \sum_v \phi_v^*(r, t) \phi_v(r', t)
\]

single particle occ. orbitals

\[
\int \hat{\mathcal{H}}(r, r', t) \phi(r', t) dr' = \left( -\frac{1}{2} \nabla^2 + \nu_H(r, t) + \nu_{ext}(r, t) \right) \phi(r, t)
\]

+ \int \Sigma(r, r', t) \phi(r', t) dr'

time-dep. perturbation, i.e. electromagn. field

self-energy

\[
\Sigma_{COH}(r, r') = \frac{1}{2} \delta(r - r') W_p(r, r')
\]

\[
\Sigma_{SEX}(r, r', t) = -\sum_v \phi_v(r, t) \phi_v^*(r', t) W(r, r')
\]

statically screened Bethe-Salpeter equation (BSE) screened Coulomb interaction
## Excited states (GW/BSE)

To correct for DFT’s band gap underestimation, quasiparticle energies can be obtained in GW approximation from

\[
\Sigma_{GW}(\mathbf{r}, \mathbf{r}'; i\omega) = \frac{1}{2\pi} \int G(\mathbf{r}, \mathbf{r}'; i(\omega - \omega')) W(\mathbf{r}, \mathbf{r}'; i\omega') d\omega'
\]

Screened Coulomb interaction required (in random phase (RPA) approx.)

\[
W(\mathbf{r}, \mathbf{r}') = \int \epsilon^{-1}(\mathbf{r}, \mathbf{r}'') v_c(\mathbf{r}'', \mathbf{r}') d\mathbf{r}''
\]

**Bottleneck:** calculation, storage & inversion of dielectric matrix is very computationally demanding, involves large sums over empty states and is hard to converge

**Solution:** spectral representation of RPA dielectric matrix; obtain matrix from directly calculating eigenvectors and eigenvalues

\[
\tilde{\epsilon} = \sum_{i=1}^{N} \tilde{v}_i \lambda_i \tilde{v}_i^H = \sum_{i=1}^{N} \tilde{v}_i (\lambda_i - 1) \tilde{v}_i^H + I
\]

\[\Rightarrow\] no summation over empty states, no inversion, storage of eigenvector/-value pairs only!
How to calculate the screening

Obtaining the eigenvectors/-values does **NOT** require explicit knowledge of the matrix; knowledge of the **action of the matrix** on an arbitrary vector is sufficient!

in linear response: \((\epsilon - I)\Delta V_{SCF} = -v_c \Delta n\)

charge density response \(\Delta n\) to perturbation of self-consist. field \(\Delta V_{SCF}\) can be evaluated from density functional perturbation theory

orthogonal iteration procedure to obtain eigenvectors/-values, using \(\Delta V_{SCF}\) as trial potentials

in RPA fast monotonous decay of dielectric eigenvalue spectrum

single parameter \(N_{eig}\) to control numerical accuracy

\[
\tilde{\epsilon} = \sum_{i=1}^{N} \tilde{v}_i \lambda_i \tilde{v}_i^H = \sum_{i=1}^{N} \tilde{v}_i (\lambda_i - 1) \tilde{v}_i^H + I
\]

[H. Wilson et al., PRB 79, 245106 (2009); D. Rocca et al., J. Chem. Phys. 133, 164109 (2010); H.-V. Nguyen et al., PRB 85, 081101 (2012)]