Electronic and Surface Structure of Group IV Nanocrystals

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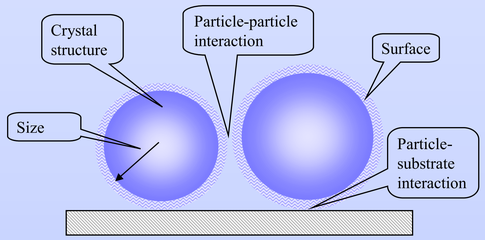
Introduction

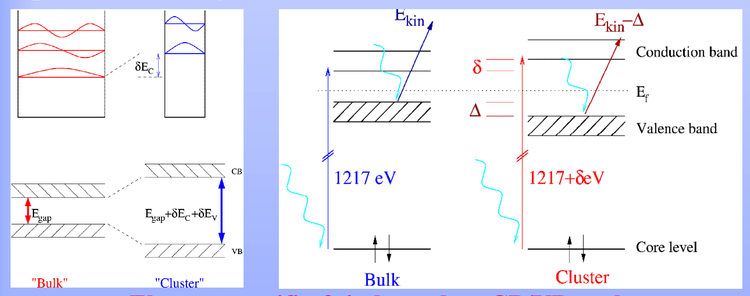
Nanocrystals exhibit novel electronic properties

- $50 < N_{atoms} < 10000$
- Structure and properties size-dependent
- Evolution of bandstructure
- Transition from nano-particle to bulk-crystal
- Electronic structure influenced by many factors



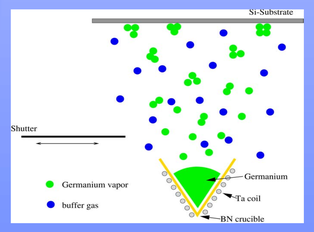
Complete understanding of structure – property relationship essential for any potential application

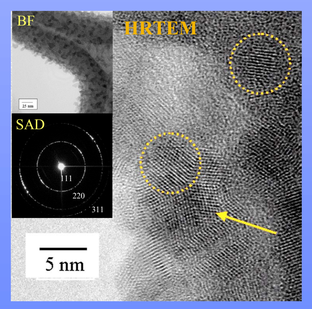
Synchrotron Radiation is a powerful tool to study deposited nanocrystals



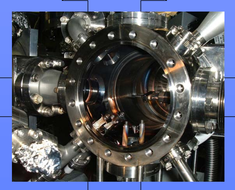
Element specific & independent CB/VB probe

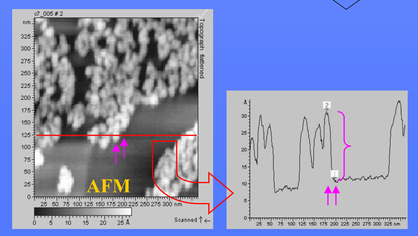
In-situ sample preparation



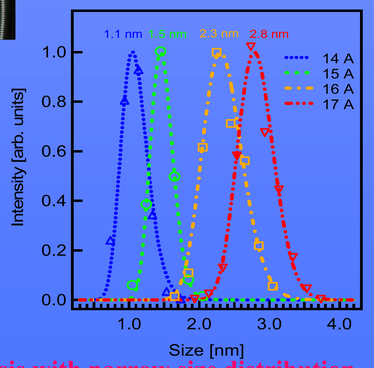


- works for virtually all elements
- wide accessible size-range
- ultra-clean production
- accessible surface chemistry





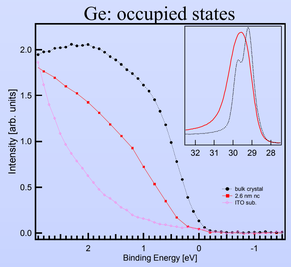
C. Bostedt, T. van Buuren, L. J. Terminello, et al., J. Phys.: Condens. Matter **15**, 1017 (2003).

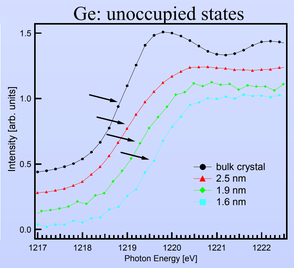


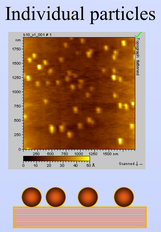
Controlled gas-phase nanocrystal synthesis with narrow size distribution

Germanium and Silicon

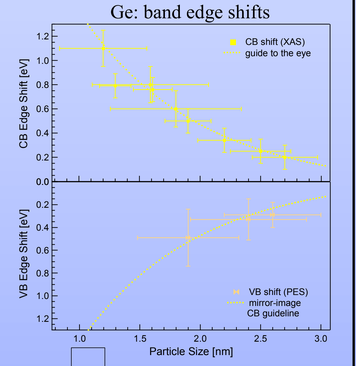
Electronic structure measured with XAS and PES:

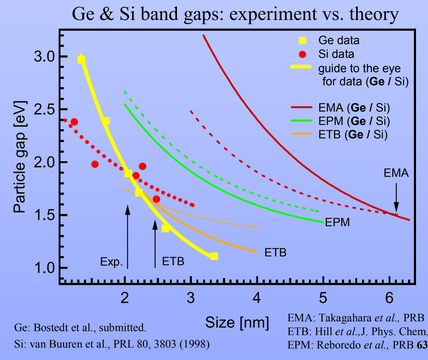






- Size-dependent CB and VB shifts
- Edge shifts are similar
- Extrapolate bandgap





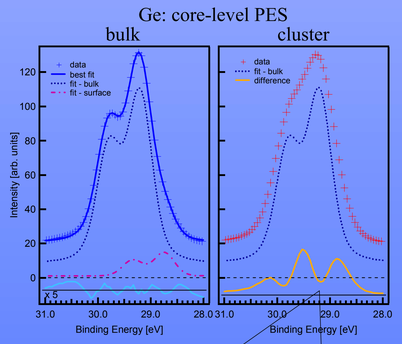
Ge: Bostedt et al., submitted.
Si: van Buuren et al., PRL 80, 3803 (1998)

EMA: Takagahara *et al.*, PRB **53**, 4205 (1996),
ETB: Hill *et al.*,J. Phys. Chem. **103**, 3156 (1999),
EPM: Reboredo *et al.*, PRB **63**, 235314 (2001)

- Ge confines stronger than Si
- Bandgap cross over around 2 nm
- Theory does not describe data well

Bandgap of Ge becomes larger than that of Si upon size reduction

Surface Structure



Distribution of surface core-level shifts

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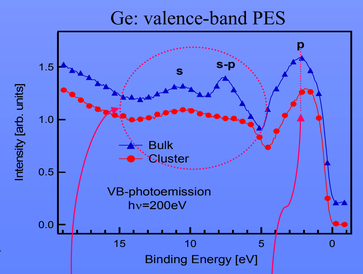
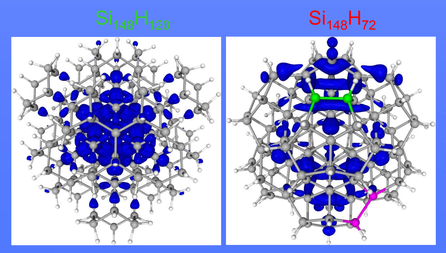
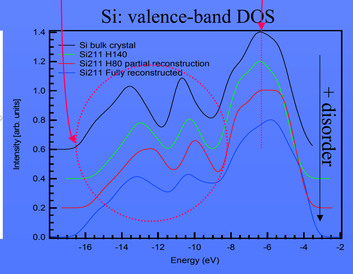
- Discrepancy between theory and experiment due to surface?
- PES – surface sensitive
- Combined experimental / theoretical approach



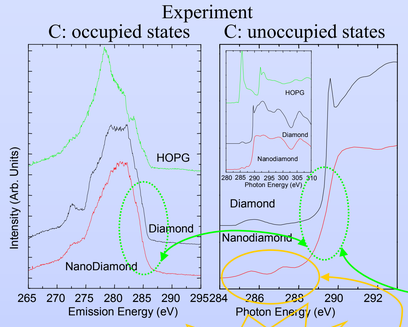


Calculations: A. Williamson, A. Puzder, G. Galli



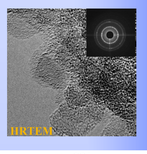
The nanocrystals exhibit a reconstructed and/or disordered surface

Diamond



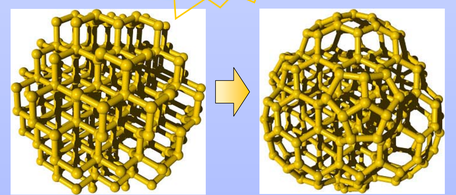
Raty, Galli, Bostedt, van Buuren, Terminello, Phys. Rev. Lett. **90**, 037401 (2003)

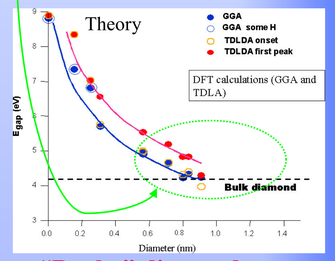
- Publication suggests huge shift for CVD grown films…?! (Chang et.al. PRL Vol. 82, p 5377 (1999))
- Combined experimental/theoretical approach
- Our experiment: individual particles with 4 nm average size
- Detonation synthesis



no shift…

…but surface reconstruction

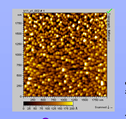


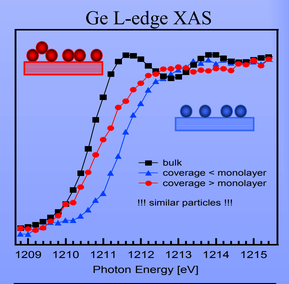


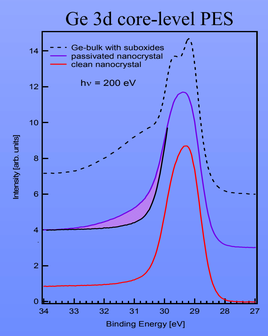
The surface fully reconstructs and forms "Bucky" diamond

Nanocrystal-Assembled Materials

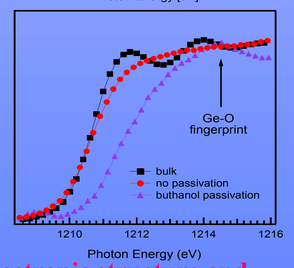
- Make use of the special properties of nanocrystals
- Produce macroscopic amounts of nanocrystals
- Investigate particle – particle interaction







C. Bostedt, T. van Buuren, L. J. Terminello, in preparation



Surface passivation key component of electronic structure and thus integration of nc-materials

Summary

- **Controlled gas-phase based synthesis method**
- **Strongest quantum confinement in Ge**
- **Band gap crossover between Ge and Si**
- **Disordered surface for Ge and Si nanocrystals**
- **Full surface reconstruction for Nanodiamond**
- **Particle – particle interaction controls properties of nanocrystal-assembled materials**

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