Cluster Approach to the Electronic Properties Modeling of Nanocrystal Structures

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Cluster approach to the electronic properties modeling of nanocrystal structures

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Outline

✓ Cluster approach for SiC electronic and vibration properties modeling
  ▪ Motivation
  ▪ Hierarchic computational approach
  ▪ Local field model

✓ TiO$_2$ electronic properties modeling using cluster approach
  ▪ Isolated TiO$_2$ clusters, N doped TiO$_2$, TiO$_2$\(\text{dye}\)

✓ Electronic properties modeling of BiVO$_4$

✓ Summary/perspectives
Silicon carbide is one of the most promising semiconductor materials for high power electronics as well as one of the best biocompatible materials due to its superior properties.

Scanning electron micrographs of MgB$_2$/SiC metamaterial [N. Limberopoulos et al. Appl. Phys. Lett. 95, 023306 (2009)]

a) PL spectra taken on both sides of the crystalline 6H–SiC wafer at 9 and 300 K. b) Low temperature PL spectra of SiC wafer (C side), nanoporous SiC, and SiC nanopowder. [Botsoa et al. J. Appl. Phys. 102, 083526 (2007)]
Investigated SiC nanoparticles have different:

- **Structure**: 3C – SiC, 6H - SiC
- **Size**: 10 – 50 nm
- **C/Si ratio**: C/Si 1.10 – 0.85

A high-resolution TEM image evidences the covering of the particle surface by carbon sheets.

Model of SiC nanograins

Cluster model
- Clusters possessing about 200 atoms
- Clusters covered with carbon

Simulated structures
- 3C-SiC and 6H-SiC ideal structures
- Partially reconstructed structure
- Amorphous structure of SiC
Test of cluster size

IR absorption spectra for 3C-SiC nanoclusters:
0.5 nm (a), 0.8 nm (b), 1.1 nm (c).

Phonon DOS for 3C-SiC nano-clusters:
0.5 nm (a), 0.8 nm (b), 1.1 nm (c).

M. Makowska-Janusik, A. Kassiba, J. Bouclé, J-F. Bardeau, S. Kodjikian, A. Désert,
IR absorption spectra for SiC nanoclusters

- SiC amorphous structure
- β-SiC defected structure

In the investigated host-guest system the SiC nanoparticles are embedded into polymeric matrix (not grafted)

Requirements:

- The wt % of SiC nanoparticles should be appropriate in order to not agglomerate (3 – 6 wt %)
- Dissolution of small molecules in host material decreases its $T_g$. There should be chosen polymers with relatively high $T_g$ and well transparent for light used in experiment
Characteristic of the host-guest silicone carbide based materials

SiC where incorporated into polymeric matrix:
- PMMA
- PVK
- PC

TEM image of the composite PVK/SiC system.
It shows the local dispersion of the nc-SiC in the polymer matrix.

Bulk system approach

Requirements:

• SiC cluster should be separated one from the other (Drude nonpolar fluid model)

• Cluster should be big enough to model influence of polymer on structural properties of dopant

• The size of SiC cluster should allow the quantum – chemical calculations of optical

Local field

\[ E_{\text{local}} = E_{\text{ex}} + E_{\text{el}} + E_{\text{d}} \]

Calculated by removing molecule and evaluating field at the point of interest from neighbour charges and dipoles surrounding this point.

Parameters of molecular dynamics simulations

Density of the simulated systems 1.20 g/cm³

PMMA 90-mer - molecular wt. 9012.58 amu
PC 50-mer – molecular wt. 12716.21 amu
PVK 50-mer – molecular wt. 9664.45 amu

SiC - 216 atoms - mass 4330.48 amu

PMMA/SiC - 48.05 wt %
PC/SiC - 34.05 wt %
PVK/SiC - 44.81 wt %

MM - molecular mechanics method

Force field - all-atom consistent valence force field (CVFF)

Boundary condition – 3D Ewald summation
Cutoff – 1.30 nm

GROMACS:
The World's fastest Molecular Dynamics - and it's GPL!
Cluster model

- Clusters possessing up to 200 atoms
- Clusters covered with carbon

Si-C distance it is intrinsic cluster property

R₁ = 1.88 Å
R₂ = 3.61 Å

S-C distances

Radial distribution function G(r)

Internal structure
last-3 shell
last-2 shell
last-1 shell
last shell

Si-C distance [nm]

Radial distribution function G(r)

Cluster model

3C – SiC

Si-C distances

R₁ = 1.88 Å
R₂ = 3.61 Å
SiC – polymer distance

The shortest distance between COM of SiC and polymer’s groups

Radial distribution function $G(r)$

Separation distance [nm]

PMMA
PC
PVK
Electro-optical properties of investigated systems

Photoluminescence spectra of 6H-SiC cluster

System parameters:
1% SiC 218/1400°C, C/Si<1, d = 39 nm

Solid-State Dye-Sensitized Solar Cells (DSC)

Hole conductor - Spiro-OMeTAD

HOMO ~ 5 eV

$T_g = 121°C$

- Allows efficient dye regeneration
- Suitable TiO$_2$ pore filling up to several mm


Indoline dye – D102

Conversion efficiency

$\eta = 7\%$

Absorption coefficient

$\mu = 55 800 \text{ L mol}^{-1}\text{cm}^{-1}$


Crystal structures of TiO$_x$
**TiO₂ and N-TiO₂ Nanoparticles**

**Synthesis by Laser pyrolysis**


**Liquid precursor** - Titanium Isopropoxide (+ C₂H₄) (aerosol)

**N-doping** : addition of NH₃

Production rate - 20g/h (lab. scale)

+ soft annealing in air at 400°C (remove C)

**TiO₂**

Wide band gap material (∆Eg > 3eV)

- Cheap – abundant – non toxic
- Leads to best performance up to now
  - > 12% in 2011 with a liquid electrolyte

< d > = 12.5 ± 2.5 nm
Anatase > 95 %

**N-TiO₂**

< d > = 7.5 ± 1.8 nm
Anatase > 95 %
N content = 0.5 at.%

Doping procedures ⇒ photo-activity in the visible

Analysis of the computational method

For the analysis the anatase structure was chosen - it has the simplest and best known structure.

Total charge density redistribution

The Ti atoms of rutile are octahedrally coordinated.

The strongly ionic character of the bonds results in localization of charge around the O$^{2-}$ anions

- The passivation procedure is important for small clusters.
- For bigger clusters all passivation methods give the same results

RUTIL
$\Delta E_{\text{HOMO-LUMO}}$ 3.06 eV experiment - bulk
3.17 eV PM7 method - cluster 1.2 nm

ANATASE
$\Delta E_{\text{HOMO-LUMO}}$ 3.20 eV experiment - bulk
3.33 eV PM7 method - cluster 1.2 nm unpassivated
The HOMO-LUMO energy gap splitting of TiO$_2$ vs cluster size

### DFT methodology with different XC potential

<table>
<thead>
<tr>
<th>Cluster size [nm]</th>
<th>BLYP</th>
<th>B3LYP</th>
<th>LC-BLYP</th>
<th>CAMB3LYP</th>
<th>LC-BLYP $\mu = 0.8$</th>
<th>$\Delta E_{\text{HOMO-LUMO}}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.97</td>
<td>1.04</td>
<td>4.63</td>
<td>2.92</td>
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<tr>
<td>0.8</td>
<td>0.77</td>
<td>0.83</td>
<td>3.62</td>
<td>2.28</td>
<td>3.97</td>
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<tr>
<td>1.0</td>
<td>0.47</td>
<td>0.50</td>
<td>2.94</td>
<td>1.85</td>
<td>3.03</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>0.42</td>
<td>0.45</td>
<td>2.91</td>
<td>1.46</td>
<td>3.03</td>
<td></td>
</tr>
</tbody>
</table>

HOMO-LUMO energy gap splitting calculated for unpassivated (TiO$_2$)$_n$ anatase cluster with diameter equal to 1.0 nm using LC-BLYP functional vs range separation parameter $\mu$

\[
E_X = E_X^{sr} + E_X^{lr}
\]

\[
\frac{1}{r_{12}} = \frac{1 - \text{erf}(\mu r_{12})}{r_{12}} + \frac{\text{erf}(\mu r_{12})}{r_{12}}
\]
The acceptor character of nitrogen

Nitrogen doping – cluster with size 1 nm
Anatase structure
HOMO-LUMO 3.06 eV
Anatase (6.45 % of N)
HOMO-LUMO 2.4 eV

The evidential influence of Nitrogen atomic orbitals on HOMO is seen for the Oxygen vacancy containing clusters

<table>
<thead>
<tr>
<th>n</th>
<th>Crystal</th>
<th>Amorphous</th>
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<tr>
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<td>53</td>
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<td>77</td>
<td>2.924</td>
<td>4.099</td>
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<tr>
<td>89</td>
<td>2.339</td>
<td>3.058</td>
</tr>
</tbody>
</table>
Electronic properties of TiO$_2$/D102 composite

HOMO (red) and LUMO (blue) orbitals redistribution for D102 dye molecule calculated by LC-BLYP functional approximation.
Computer simulations of the Bi$_2$O$_3$ and the BiVO$_4$ electronic properties

BiOV$_4$ starting from $n=20$ has 2.93 eV
Experimental value 2.40 - 2.50 eV

Bi2O3 starting from $n=50$ has 2.01 eV
Experimental value 2.58 - 2.85 eV
Conclusions

- Electronic properties of isolated nanoparticles may be calculated using the cluster approach applying the discrete local field approximation.

- Covalently bounded atoms like SiC or BiVO₄ nanoparticles may be calculated using *semi*-empirical or DFT theory.

- TiO₂ is the ionic crystal and the LC methodology should be used for the suitable calculations.

- The surface passivation and the surface reconstruction is important for the SiC calculations and should be important for all covalently bounded nanostructures.

- The TiO₂ as the big nanoparticles may be computer without any defined surface properties.