

Ab initio investigations on the electronic and optical properties of group IV semiconductor nanocrystals

PH.D. THESIS BOOKLET

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(2013)

Introduction

Semiconductor nanocrystals are nanometer sized crystals that originate from semiconducting bulk materials. The properties of nanocrystals are mostly governed by the fact that their size is in the range where quantum mechanical effects are very important. This has crucial effects, e.g. contrary to the indirect band structure of micrometer sized crystallites, nanocrystals may have measurable luminescence. Furthermore, the surface bears special importance due to the large surface/volume ratio. Its presence can completely change the behavior of the system, overcoming the quantum confinement effect. On one hand, this is a drawback since one has to be extremely cautious when it comes to making nanocrystals, on the other hand this unique property gives new knobs to turn: by changing the ligands at the surface or by manipulating surface atoms one may readily tune the properties of nanocrystals towards the desired direction.

Thanks to the ever improving experimental techniques, producing and working with nanocrystals can be done routinely in the laboratories nowadays. Semiconductor nanocrystals are important target materials for realizing chemical, biological sensors and third generation solar cells. Since only indirect measurements can be done on these deeply quantum mechanical objects in most of the cases, it is inevitable to perform atomistic simulations.

Goals of the research

My research is devoted to the investigation of the optical properties of group IV semiconductor nanocrystals using density functional theory and beyond methods. Since I dealt with covalently bonded nanocrystals in my work, the surface is of special importance: the symmetry is broken, atoms have dangling bonds that have to be considered. Understanding the behavior of such surface structures is one of the most important aspect both from experimental and theoretical point of view. It is more and more important to not only understand already existing experiments, but also to predict new working principles.

My work can be partitioned into three major areas following how one can make nanocrystals based on carbon and silicon: I have investigated the optical properties of silicon, silicon carbide, and diamond nanocrystals.

- Third generation solar cells hold the promise for cheaper and more efficient photovoltaics than existing solutions. According to the Shockley–Queisser limit, the overall efficiency of single junction solar cells is limited by the fact that highly energetic excited charge carriers relax to their respective band edges via phonon emission. Avoiding phonon assisted relaxation may result in either *hot electron* or *carrier multiplication* solar cells. In the former the photovoltage while in the latter the extracted current is increased. Considering the latter, quantum confined structures may help increasing carrier multiplication events yielding higher quantum efficiency as was originally suggested by theoretical

predictions, which has been experimentally confirmed. Interestingly, first experimental reports were hard to reproduce. I set the goal to investigate high energy excitations in silicon nanocrystals as a function of surface terminations and to correlate the results with available experimental data.

- Silicon carbide nanocrystals are potential candidates for realizing *in vivo* biological imaging. Results published in the literature regarding the optical properties of silicon carbide nanocrystals were controversial: the optical gap of larger nanocrystals was larger, which contradicts quantum confinement – the smaller the nanocrystal the larger the gap. My goal was to resolve this controversy by modeling.
- Diamondoids, special diamond nanocrystals built up from the diamond cages are sp^3 bonded structures. According to recent experiments 99% pure diamond nanocrystal samples can be produced with knowing their exact atomic structure. It was not experimentally understood what was the reason for their relatively low optical gap, as confinement predicts that it would be beyond 10 eV. Furthermore, the size and optical gap relation was not monotonous. Since the structure of these nanocrystals is exactly known, they are ideal testbeds to benchmark theoretical approaches. My goal was to understand these issues by performing density functional theory based calculations. Further calculations could be carried out to investigate the effect of surface adsorbants as the surface is very well controllable using standard chemistry approaches, for example. This may be useful to achieve bioimaging of human cells. However, pure diamondoids luminesce in the ultraviolet range, for bioimaging applications light emission in the infrared range is sought after. I set forward calculations to find ligands that tune the optical properties towards the desired visible, infrared range.

Methods

Calculating the optical response of semiconductor nanocrystals is far from being trivial, even with current computational capacities. Since the quantum mechanical nature of electrons cannot be neglected, the Schrödinger equation in its full realm needs to be addressed. Within linear response theory, the knowledge of the energies and wave functions of the ground and excited states of time-independent Schrödinger equation is enough, one can then easily obtain the expectation values of spectroscopic observables using well-known formulas. However, the solution of the Schrödinger equation is not possible but for very small systems, which are of no real interest in real physical situations.

In order to arrive at approximate solutions of the Schrödinger equation, I have used a different formulation of Schrödinger's wave function theory, which became famous as "density functional theory". In density functional theory the main variable is not the many-body wave function, but the three-dimensional density, as its name suggests [[Hohenberg and Kohn, 1964](#)].

This reduction of the phase-space is very good for numerical reasons, still all effects previously included in the wave function has to be wrapped into an effective field (exchange-correlation potential) [Kohn and Sham, 1965]. This effective field is not known exactly, but there are numerous ways to approximate it. The statistically accurate PBE0 approximation (so called hybrid functional) was proven to be one of the most accurate approach without any empirical parameters [Burke et al., 1997, Adamo and Barone, 1999].

During my work, I used this particular functional and its predecessor, the PBE functional. To predict the optical properties of nanocrystals I used the linear-response formulation of time-dependent density functional theory, which is an extension of *ground state* density functional theory to treat time-dependent problems [Runge and Gross, 1984].

New scientific results

- 1. First Thesis point** My time-dependent density functional theory calculations showed that: (a) 2×1 -like surface reconstruction decreases the optical gap (E_g) of the $d=1.2$ nm hydrogenated silicon nanocrystal from 3.0 eV to 2.0 eV, furthermore it yields enhanced absorption in the $0 - 2 \times E_g$ region. The $d=2$ nm nanocrystal showed no gap reduction upon 2×1 -like reconstruction, but the absorption was increased in the $0 - 2 \times E_g$ region due to enhanced density of states around band edges. (b) In case of 25% surface coverage the presence of surface methyl groups give rise to 45(10)% increase in the integrated absorption in the $0 - 2 \times E_g(0 - 3 \times E_g)$ region. The presence of surface hexyl groups with 19% surface coverage yields 100(60)% increase in the respective energy regions. (c) By increasing the concentration of silicon nanocrystals, the absorption gets enhanced in the $0 - 3 \times E_g$ energy region due to overlapping unoccupied states. These findings explain recent experimental measurements where increased absorption was measured with increasing nanocrystal concentration and may help optimize nanocrystal based photovoltaic cells[T1].
- 2. Second Thesis point** I showed that the calculated optical gap of hydrogenated silicon carbide nanocrystals with diameter of 0.9–3.2 nm can be described by the equation $E(d) = 1.41 + 2.74/d^{1.34}$, where E is given in eV and d is the diameter of the nanocrystals in nanometer. Furthermore, I showed that 2×1 , 3×1 and step like surface reconstructions give rise to defect states within the gap for smaller than ≈ 3 nm nanocrystals [T2,T3,T4].
- 3. Third Thesis point** I showed by means of time-dependent density functional calculations on the 1.4 nm silicon carbide nanocrystals that some specific oxygen related defects significantly alter the optical and vibrational properties: (a) The neutral C=O double bond shrinks the optical gap the most: the gap decreases from 4.2-4.3 eV (ultraviolet region) to 1.8-1.9 eV (red part of the visible region). I found that the calculated characteristic C=O stretching bond is at 1650 cm^{-1} . (b) The neutral Si=O double bond has a

calculated stretching mode of 1250 cm^{-1} and an absorption edge of 2.8 eV . These results explain well experimental findings[T4,T5,T6].

4. **Fourth Thesis point** My time-dependent density functional theory calculations with the PBE0 hybrid functional kernel on 10-26 atom diamond nanocrystals (diamondoids) showed that (a) the lowest energy excited states are Rydberg-like states for all the considered structures with showing practically no quantum confinement; (b) the calculated optical gaps are in agreement with the experimental findings with mean absolute deviation of 0.15 eV ; (c) the calculated optical gaps show non-monotonous behavior as a function of the number of carbon atoms in the system which is due to dipole forbidden optical transitions in diamantane, [121]tetramantane, [12312]hexamantane[T7,T8].
5. **Fifth Thesis point** My time-dependent density functional theory calculations showed that if hydrogen atoms are replaced by double bonded sulfur atoms on the surface of two selected diamondoids (adamantane and [1(2,3)4]pentamantane) then the optical gap is pushed towards the visible region. I found that at full surface coverage the energy of the first dipole allowed optical transition is 2.6 eV for adamantane and 1.5 eV for [1(2,3)4]pentamantane. The transitions responsible for the gap shrinkage are $n \rightarrow \pi^*$ transitions. This finding, together with the biocompatibility of diamond, may help in realizing new generation of *in vivo* biological markers[T8,T9].

Publications related to the thesis points

[T1] High Energy Excitations in Silicon Nanoparticles

Adam Gali, Márton Vörös, Dario Rocca, Gergely T. Zimanyi, and Giulia Galli

Nano Letters **9**, 3780-3785 (2009)

[T2] The absorption spectrum of hydrogenated silicon carbide nanocrystals from *ab initio* calculations

Márton Vörös, Péter Deák, Thomas Frauenheim, Adam Gali

Applied Physics Letters **96**, 051909 (2010)

[T3] Time-dependent density functional calculations on hydrogenated silicon carbide nanocrystals

Márton Vörös, Péter Deák, Thomas Frauenheim, Adam Gali

Mater. Sci. Forum **679 - 680**, 516 (2011)

[T4] Electronic and optical properties of silicon carbide nanotubes and nanoparticles studied by density functional theory calculations: effect of doping and environment

Márton Vörös, Adam Gali

Journal of Computational and Theoretical Nanoscience **9**, 1906 (2012)

[T5] The absorption of oxygenated silicon carbide nanoparticles

Márton Vörös, Péter Deák, Thomas Frauenheim, Adam Gali

The Journal of Chemical Physics **133**, 064705 (2010)

[T6] Influence of oxygen on the absorption of silicon carbide nanoparticles

Márton Vörös, Péter Deák, Thomas Frauenheim, Adam Gali

Mater. Sci. Forum **679 - 680**, 520-523 (2011)

[T7] Optical absorption of diamond nanocrystals from *ab initio* density-functional calculations

Márton Vörös and Adam Gali

Physical Review B **80**, 161411(R) (2009)

[T8] The Absorption of Diamondoids from Time-dependent Density Functional Calculations

Márton Vörös, Tamás Demjén, Adam Gali

MRS Spring Meeting Proceedings, 1370: mrss11-1370-yy02-07 (2011)

[T9] Tuning the optical gap of nanometer-size diamond cages by sulfurization: A time-dependent density functional study

Márton Vörös, Tamás Demjén, Tibor Szilvási, Adam Gali

Physical Review Letters **108**, 267401 (2012)

Other publications

[O1] Annealing Simulations to Determine the Matrix Interface Structure of SiC Quantum Dots Embedded in SiO₂

Jan Knaup, [Márton Vörös](#), Péter Deák, Adam Gali, Thomas Frauenheim, Efthimios Kaxiras
Phys. Status Solidi C **7**, 407 (2010)

[O2] Identification of defects at the interface between 3C-SiC quantum dots and a SiO₂ embedding matrix

[Márton Vörös](#), Adam Gali, Efthimios Kaxiras, Thomas Frauenheim, Jan Knaup
Phys. Status Solidi B **249**, 360 (2012)

[O3] High-Pressure Core Structures of Si Nanoparticles for Solar Energy Conversion

Stefan Wippermann, [Márton Vörös](#), Dario Rocca, Adam Gali, Gergely T. Zimanyi, and Giulia Galli
Physical Review Letters **110**, 046804 (2013)

[O4] Increasing impact ionization rates in Si nanoparticles through surface engineering: A density functional study

[Márton Vörös](#), Dario Rocca, Giulia Galli, Gergely T. Zimanyi, and Adam Gali
Physical Review B **87** 155402 (2013)

[O5] Optically Controlled Switching of the Charge State of a Single Nitrogen-Vacancy Center in Diamond at Cryogenic Temperatures

P. Siyushev, H. Pinto, [Márton Vörös](#), Adam Gali, F. Jelezko, and J. Wrachtrup
Physical Review Letters **110** 167402 (2013)

[O6] Molecular-sized fluorescent nanodiamonds

Igor I. Vlasov¹, Andrei A. Shiryaev, Torsten Rendler, Steffen Steinert, Márton Vörös, Fedor Jelezko, Anatoly V. Fisenko, Lyubov' F. Semjonova, Oleg .I. Lebedev, Ilmo Sildos, Philip. R. Hemmer, Vitaly I Konov, Adam Gali and Jörg Wrachtrup
Nature Materials, submitted

[O7] Germanium nanoparticles with high pressure core structures for third generation photovoltaics: a density functional study

[Márton Vörös](#), Stefan Wippermann, Dario Rocca, Adam Gali, Gergely T. Zimanyi, and Giulia Galli
in preparation

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- W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, 140:A1133–A1138, Nov 1965. [3](#)
- Erich Runge and E. K. U. Gross. Density-functional theory for time-dependent systems. *Phys. Rev. Lett.*, 52:997–1000, Mar 1984. [3](#)