Variation and adjustment of the optical gap of small Si nanocrystals by partial substitution of Si with Ge

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Abstract. In order to adjust the optimum region of diameters of Si based nanocrystals, which can emit in the visible region of the spectrum, we have partially substituted in Si nanocrystals layers of Si atoms by similar layers of Ge atoms and calculated the optical and HOMO-LUMO gaps as a function of Ge concentration and of the size of the nanocrystals, up to about 20Å in diameter. For the calculation of the optical gap of SiₓGey:Hₜ nanocrystals as a function of x, y, and z, we have used the framework of Time Dependent Density Functional Theory (TDDFT) with the hybrid nonlocal exchange-correlation functional of Becke, Lee and Yang (B3LYP). Our results show that by proper adjustment of x y and z we can optimize either the range of diameters for a desired gap, or the value of the optical gap for a given diameter.

1. Introduction
The visible photoluminescence of porous Silicon (p-Si) and silicon nanoparticles (from which it is composed) has attracted a lot of attention in recent years, both experimentally and theoretically [1-7]. A large portion of this work has been devoted to understanding the visible photoluminescence of this material and correlating its spectrum with the diameter of the nanoparticles (or equivalently, the porosity of p-Si). It is widely accepted and well established now [4-6] that the luminescence in the visible of oxygen-free Si nanocrystals (of well defined diameter), is mainly due to quantum confinement of the corresponding nanoparticles. This is also true for Ge nanoparticles [7].

Thus, porous silicon (composed of Si nanocrystals) or Si nanocrystals by themselves, offer the possibility of intense tunable photoluminescence (PL). By varying the diameters of the nanocrystals (or equivalently the porosity of porous silicon) intense PL can be obtained across the visible spectrum, which could never take place for bulk crystalline silicon with a band gap of 1.2 eV (see figures 1 and 2). Quantum confinement is responsible for the opening of the gap from the bulk value of 1.2 eV to values of 2-3 eV (for larger nanocrystals) up to 6-7 eV for smaller nanocrystals [4-5]. This over-opening of the gap for small size nanocrystals obviously is equally undesirable as the shrinking of the gap (in bulk Si).

This problem at small sizes of nanocrystals is not so strong for Ge nanocrystals [7] because of the smaller band gap of bulk Ge, compared to Si. Even in this case, the possibilities of adjusting the optical gap (and the band gap) are limited only to proper size selection. The possibility of combining the advantages of Si (not only in the optical, but also in the electronic and technologically useful properties) with those of Ge is an intriguing and very promising project. Needless to say, that, not only the minimum critical diameter of the nanocrystals for visible PL is important, but also the maximum possible diameter.

With this in mind, we have examined the optical and electronic properties of mixed nanocrystals of the form SiₓGey:Hₜ, where all variables x, y and z have been varied within the symmetry restrictions

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and the current limitations of our computational system. It should be noted that up to date no such high level calculations exist for such systems. It should be mentioned that even for the optical properties of pure Ge nanocrystals, besides our recent work [7], only semiempirical methods, or simple local density (LDA) ground state calculations exist (without gradient corrections) [7].

2. Outline of the calculations
In this work, as in our previous studies [4-7], we have performed ab initio calculation of the optical gap of small Ge nanocrystals based on Time Dependent Density Functional Theory (TDDFT) employing the hybrid nonlocal exchange-correlation functional of Becke and Lee, Yang and Parr (B3LYP) [4-7]. The accuracy of these calculations (TDDFT/B3LYP) for the optical gap has been tested before by high level multireference second-order perturbation theory (MR-MP2) for the case of Si nanocrystals, with excellent results [4].

As in our previous work [6-7], the size of the nanocrystals considered here ranges from 5 to about 20 Å. This corresponds to values of $x$ and $y$ from 5 to 99 Si or Ge atoms and to values of $z$ between 12 and 100 H atoms (a total of about 199 atoms). High level calculations of this type are accompanied with a computational cost which currently prohibits expansion of these calculations to much larger systems. The symmetry of the nanocrystals is $T_d$ and their geometries have been fully optimized within this symmetry constrain using the hybrid B3LYP functional. The choice of this functional is of critical importance for the good accuracy of our results. The DFT and the TDDFT calculations were performed with the TURBOMOLE [6] suite of programs using Gaussian atomic orbital basis sets of split valence [SV(P)]: [4s3p1d]/[2s] quality [9].

3. Results and discussion
In figures 1 and 2 we display the HOMO-LUMO and the fundamental optical gap respectively, for Si and Ge nanoparticles of diameters, up to around 20 Å. As we can see in these figures there is an inverse correlation of the optical gap (and the “band gap”) with the size of the nanoparticle, as is well known [1].

Figure 1. Comparison of the HOMO-LUMO gap for Si$_x$:H and Ge$_y$:H nanocrystals, as a function of their diameter.

Figure 2. Comparison of the fundamental optical gap of Si$_x$:H and Ge$_y$:H nanocrystals, as a function of their diameter.

Figure 3 is an expected natural extension of figure 2. The optical gaps of the Si$_x$:H nanocrystals for a given diameter (and thus, for a given total number of atoms $x+y$) actually, as expected, fill all the space between the two curves of figure 2, depending on the values of $x$ and $y$ (with $x+y =$ constant). For this figure we have chosen $x = y$. 
In figure 4 we have plotted the HOMO-LUMO gap for various configurations, i.e. relative number of Ge/Si atoms \([\text{Ge atoms/}(\text{Ge atoms} + \text{Si atoms})]\), as well as total number of atoms (Si+Ge). As we can see in this figure, even the points corresponding to the same total number of atoms cannot be connected with a fully continuous line, but rather with two almost parallel straight lines. Apparently, the reason is that the different points (with the same total number of atoms) correspond to different relative spatial configurations of Ge/Si atoms, i.e. Ge substitution of Si at different layers relative to the surface of the nanocrystal.

To verify this, we have plotted in figure 5 for given total number of Si+Ge atoms (here \(x+y=71\)) the binding energy (atomization energy) of the various nanocrystals as a function of the number of the substituting Ge atoms. As we can see, we have two distinct curves (parallel lines) depending on the exact location of the Ge layer, relative to the surface of the nanocrystals. It is clear that it is preferable to have the heavier Ge atoms in the “inner” part of the nanocrystal. Therefore, it is not surprising that the data of figure 4, for a constant total number of atoms, are not lying in one continuous line.

In figure 6, we display the variation of both HOMO–LUMO gap and the fundamental optical gap of a medium size nanocrystal \((x+y=47)\) as a function of the number of Ge atoms. As explained above, due to the fact that we have different number and spatial configurations of Si and Ge atoms in the nanocrystals, the data points cannot be connected with a continuous line. The difference in energy between the two sets of points, which can be considered as the exciton binding energy \((E_B)\), is practically constant, between 0.5-0.6 eV. This of course could be anticipated from figures 1 and 2. For larger nanocrystals, \(E_B\) approaches 0.45 eV. This is expected by the quantum confinement hypothesis, according to which \(E_B\) must decrease as the diameter of the dot increases.
Figure 6: Variation of the HOMO-LUMO and the optical gap as a function of the number of Ge atoms in the nanocrystals Si$_{65}$Ge$_{x}$:H, Si$_{36}$Ge$_{35}$:H, and Si$_{5}$Ge$_{65}$:H nanocrystals.

Finally, to facilitate the comparison of the electronic structure (“band structure”) of the nanocrystals, for different concentrations of Ge atoms, we have plotted in figure 7, the electronic density of states (DOS) for three typical nanocrystals (one Si-rich, one Ge-rich and one of about equal concentrations of Si and Ge). The DOS curves were generated from the eigenstates of the ground state calculations with a suitable gaussian broadening. As we can see, the largest variation with the Ge concentration occurs in the valence band edges, while the conduction band edge is relatively insensitive.

4. Conclusions
We have shown that, indeed, the mixed SiGe nanocrystals have optical and electronic properties intermediate between those of pure Si and Ge nanocrystals. The large variety of optical and band gaps depends, not only on the relative concentrations, but also on the relative spatial distribution of the Ge atoms with respect to the surface of the nanocrystals. This work is in progress.

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