Microelectronic Engineering xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Size dependence of the optical gap of "small" silicon quantum dots: *Ab initio* and empirical correlation schemes

Shanawer Niaz [b], Emmanuel N. Koukaras [b], Nikolaos P. Katsougrakis [a], Theodoros G. Kourelis [a], Dimitrios K. Kougias [b], Aristides D. Zdetsis [b,*]

[a] Division of Medical Physics, School of Medicine, University of Patras, Patras GR-26500, Greece
[b] Molecular Engineering Laboratory, Department of Physics, University of Patras, Patras GR-26500, Greece

ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Quantum Dots
Silicon
Density Functional Theory
Quantum Confinement
bond-order-length-strength

ABSTRACT

We present a comparative study of the energy-gap dependence on diameter d of "small" ($d < 20$ Å) hydrogen-terminated Si quantum dots, using density functional theory (DFT) with the hybrid functional of Becke, Lee, Parr and Yang (B3LYP). These accurate real space *ab initio* calculations [see [1], Garoufalis et al., Phys. Rev. Lett. 87 (2001) 276402] are used to compare the size dependence of the band gap according to quantum confinement theory in relation to the empirical bond-order-length-strength (BOLS) correlation mechanism, usually applied to larger nanocrystals. Our results for the gap variation, in the range of diameters considered here, are in very good agreement with quantum confinement theory and they reproduce by extrapolation the experimental band gap of bulk silicon with high accuracy (error smaller than 1%). On the contrary, extrapolation of fitted band gaps by BOLS scheme, grossly overestimates the band gap of bulk (by almost 80%); whereas, forcing the agreement of bulk band gap results in largely underestimated dot band gaps, in the range of diameters considered here.

1. Introduction

The visible photoluminescence (PL) of silicon quantum dots or silicon nanocomposed structures, such as of porous Silicon (p-Si) has attracted a lot of attention in recent years, both experimentally and theoretically [1–6]. Numerous applications of silicon quantum dots (QDs) for optical devices such as light emitting devices [7], photovoltaic cell [8] and biocompatible luminescent silicon quantum dots [9] have been developed.

A critical quantity for most applications is the band gap variation with size for various regions of sizes. Several models have been proposed in the early literature for the band gap variation with size, such as quantum confinement (QC) [10–14], free-exciton collision [15], impurity luminescent centre [16] mechanism and the empirical bond-order-length-strength (BOLS) correlation mechanism [17–19].

Most of the work in this field has been devoted to understanding the visible photoluminescence of the QDs and correlating the spectrum with the diameter of the quantum dots. It is widely accepted now [4–6] that the luminescence in the visible of oxygen-free small Si quantum dots (of well defined diameter), is mainly due to quantum confinement of the corresponding quantum dots [1]. However, several times, other alternative mechanisms, such as the ones mentioned above have been also considered for the description of the detailed variation of the gap with the size (diameter) of the dots.

Knowledge of the detailed size variation of the gap, especially in a large range of sizes (hopefully approaching macroscopic sizes) is essential for "band gap engineering" and for the design of tunable photoluminescence.

In our present work we examine in detail the functional dependence of the energy gap on the basis of very accurate *ab initio* DFT calculations based on the B3LYP functional [1] in the range of about 10–20 Å, which is expected to be dominated by quantum confinement. We have paid special attention not only in the basic approximations but also in the technical details (quality of the basis set, mesh of integration, etc.) as is described in the technical details (Section 2). To extrapolate these results to larger diameter scales, dominated usually by empirical schemes, we have fitted our DFT gap-versus-size results according to the predictions of two representative but "extremely opposite" (both in philosophy and in principles) methods: The "*ab initio* based" Quantum confinement theory, and the empirical scheme known as the bond-order-length-strength (BOLS) correlation mechanism [17–19]. As will be shown below, QC not only fits perfectly the DFT/B3LYP results in the region of 10–20 Å, but also predicts with unexpected accuracy the extrapolated band-gap of the infinite size crystal. On the contrary, BOLS scheme can be fitted or fixed to describe only one region of diameters, but not both, and certainly not

* Corresponding author. Tel./fax: +30 2610 997458.
E-mail address: zdetsis@upatras.gr (A.D. Zdetsis).

0167-9317/$ - see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.mee.2013.07.005

all. This could be expected, especially for the region of our present QDs, which are smaller than 2 nm, in the region dominated by strong quantum confinement.

2. Technical details of calculations

In this work we present *ab initio* calculations of electronic optical and structural properties (using geometry optimization) based on the DFT/B3LYP method, employing the hybrid nonlocal exchange–correlation B3LYP functional [20]. This functional has been shown to efficiently reproduce the band structure of a wide variety of materials, including c-Si, with no need for further numerical adjustments [21]. Zdetsis et al. [22] reported indirect band gap of 3.5 eV, using B3LYP formalism. The size of the quantum dots considered here ranges from 5 to 147 atoms, with 12–100 H atoms (a total of 247 atoms). The diameter of the larger cluster which is 18.36 Å, included in this study is $Si_{147}H_{100}$. All dots have T_d symmetry, their geometries have been fully optimized within this symmetry constraint, using the hybrid B3LYP functional [20]. The optimized structures of the quantum dots considered here are shown in Fig. 1.

The DFT calculations were performed with the TURBOMOLE [23] suite of programs using Gaussian atomic orbital basis sets of split valence [SVP], TZVP (and in some cases def2-TZVPP quality for both silicon and hydrogen) [24]. The SVP basis set was used for the optimization of the larger dots (for computational economy), after which single point calculations of the energy were performed with the TZVP basis. We have also tested (in the calculations of binding energy of the larger dots) for possible basis set superposition error by using the Counterpoise method [25]. Convergence criteria for the SCF energies and for the electron density (rms of the density matrix), were placed at 10^{-7} au, whereas for the Cartesian gradients the convergence criterion was set at 10^{-4} au.

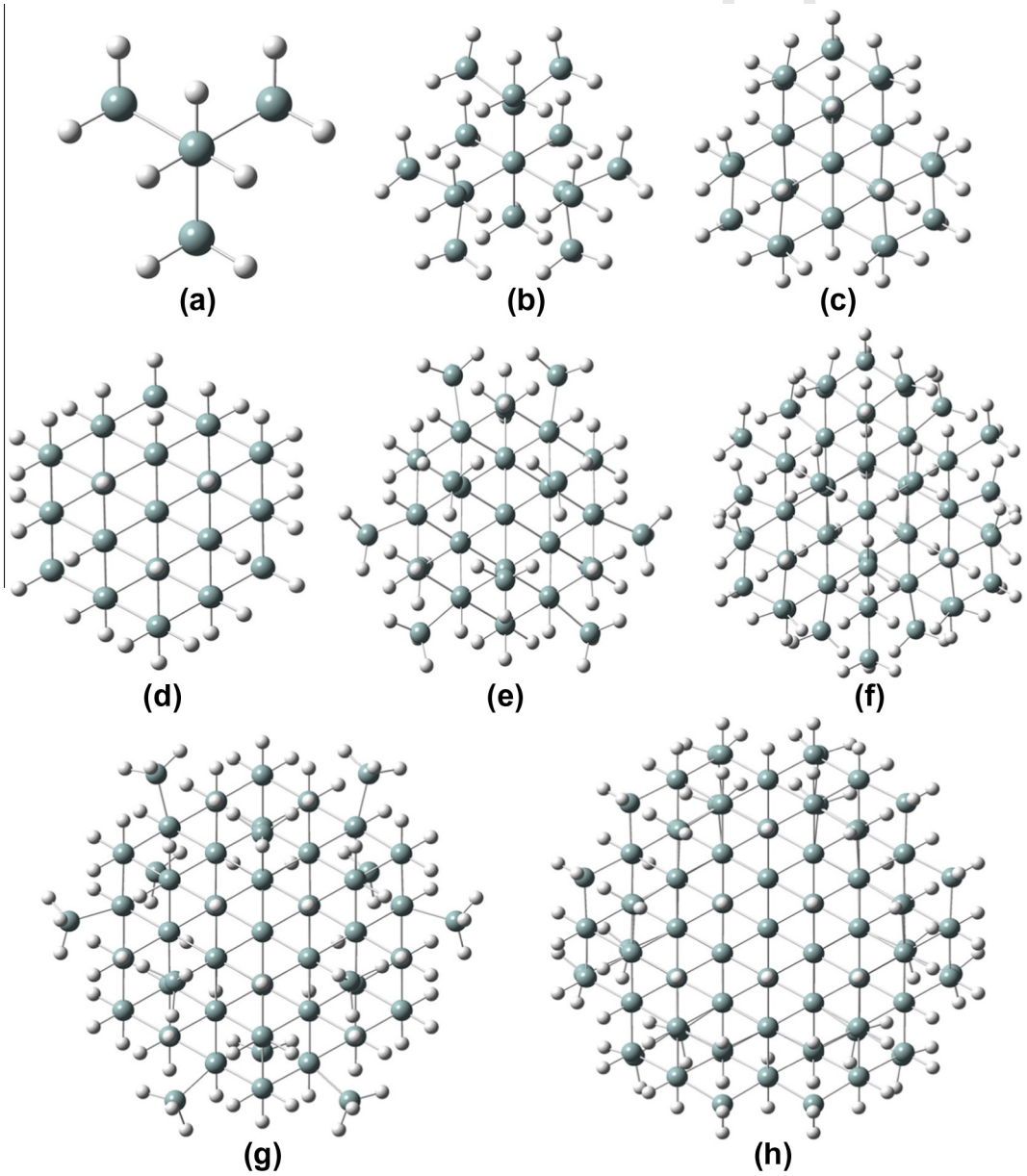

Fig. 1. Some representative Si:H quantum dots, (a) to (h) corresponds to Si_5H_{12}, $Si_{17}H_{36}$, $Si_{29}H_{36}$, $Si_{35}H_{36}$, $Si_{47}H_{60}$, $Si_{71}H_{84}$, $Si_{99}H_{100}$ and $Si_{147}H_{100}$ quantum dots ranges from 6.4 Å to 18.4 Å diameter.

Please cite this article in press as: S. Niaz et al., Microelectron. Eng. (2013), http://dx.doi.org/10.1016/j.mee.2013.07.005