Solar Energy Materials & Solar Cells 120 (2014) 622–630

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

# Surface passivation effects on the electronic and optical properties of silicon quantum dots

A. Laref [a,b,*], Noura Alshammari [c], S. Laref [d], S.J. Luo [e]

[a] Department of Physics and Astronomy, Science Faculty, King Saud University, Riyadh 11451, Saudi Arabia
[b] Department of Physics, National Taiwan University, Taipei 106, Taiwan
[c] Physics Department, University of Hail, Hail, Saudi Arabia
[d] Université de Lyon, Institut de Chimie de Lyon, Laboratoire de Chimie, Ecole Normale Supérieure de Lyon, 46 Allée d'Italie, F-69364 Lyon Cedex 07, France
[e] Department of Basic Sciences, Hubei Automotive Industries Institute, Hubei 442002, China

ARTICLE INFO

*Article history:*
Received 1 October 2012
Received in revised form
17 September 2013
Accepted 3 October 2013
Available online 7 November 2013

*Keywords:*
Surface passivation
Optoelectronic
Si quantum dots
Photovoltaic
Electronic structure

ABSTRACT

First principles calculations are carried out for investigating effect of dot-size and hydrogen passivation in silicon (Si) quantum dots. In this work, the electronic and optical properties of pure and hydrogen passivated Si quantum dots are explored. However, the importance of quantum confinements and hydrogen terminated surface on the energy gaps and optical absorption are discussed. Our results exhibit that the hydrogenated surface can cause modification in the electronic structure of Si quantum dot. It is found that the band gap increases as a function of size reduction in both passivated and unsaturated Si quantum dots because of quantum size effects. For the passivation of surface dangling bonds with hydrogen atoms, the energy gap is larger than that of pure Si quantum dots. Passivation with hydrogen atoms has a significant effect on the spatial distribution of the highest-occupied and lowest-unoccupied molecular orbitals. The impact of hydrogenation and dot-size on the optical absorption spectra and static dielectric constant is also inspected. Precisely, the dependence of dot-size and hydrogen passivation on the absorption threshold is elucidated. We surmise that this theoretical contribution can be valuable in discerning the microscopic processes for the future realization of nano-optoelectronic devices.



## 1. Introduction

With the recent breakthrough in nanotechnology, semiconductor nanostructures have indeed acquired great deal of concern in both theoretical and experimental realizations. Accordingly, the challenge is to produce functional nanomaterials with a confined size distribution, and eventually to clarify the correlations between size, shape, properties, and interfacing with the substrate. The synthesis of nanomaterials with tunable dimensions, structure, and orientation on the substrate is becoming nowadays feasible. Usually, the physical properties of nanomaterials are controlled through the modification of particle size, which yield the engineer to design the growth process according to the prerequisites and fascinating applications of the final nanodevice. This indicates that nanomaterials may display some appealing properties which are not recognized to the bulk material. Exclusively, semiconductor quantum dots (QDs) have received extensive attention because their modern technological applications can realize the physics of zero-dimensional structures. Then, it is imperative to scrutinize the physical properties of these outstanding nanomaterials, such as semiconductor QDs [1–3]. Intriguingly, they are promising because of their exceptional electronic and optical properties that can be modified artificially. In this regard, these semiconductor QDs exhibit quantum confinement effects which depend on the size and shape of structure. Among these prosperous systems, Si nanostructures have proved their potential applications in advanced optoelectronic and nano-electronic devices [4–6]. A dramatic alteration is expected in the electronic and optical properties of size-reduced Si nanostructures [7–9] since their bulk form is a semiconductor (band gap equal to 1.1 eV). It is inevitably known that silicon can emit and absorb visible light if its size is reduced to nanometer scale below its exciton Bohr radius (5 nm). For instance, silicon nanostructures may attain distinct properties as a function of size. Essentially, the drastic enhancement of photoluminescence (PL) in porous silicon can be interpreted in terms of simple quantum confinement effects [10–13]. Subsequently, this can conduct to high-performance photo-luminescent silicon nanostructures. Diverse advanced researches have been directed toward the luminescence properties of Si QDs [11–13]. For both basic comprehension and practical application of Si QDs, a profound analysis of their optical properties is mandatory. Thus, it has been detected experimentally that the optical properties of Si quantum dots are significantly

* Corresponding author at: King Saud University, Department of Physics and Astronomy, Science Faculty, Riyadh 11451, Saudi Arabia. Tel.: +966 590864930.
*E-mail address:* amel_la06@yahoo.fr (A. Laref).

0927-0248/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.solmat.2013.10.005

affected by quantum confinement effects. Meanwhile, both shape and size are crucial for modulating the optical gap of Si QDs. So, the optical properties of silicon would be considerably modified at nanoscale dimensions: With the variation of dot-size, the band gap in silicon is blue shifted from the infra-red to the optical regime. After the exploration of visible photoluminescence in porous silicon and in silicon nanostructures [10,11], the feasibility of controlling the optical response of Si nanosized systems as a function of size has turned into one of the most challenging aspects of the current silicon based nanotechnologies [12].

The recent theoretical and experimental works have demonstrated that hydrogen terminated surface can profoundly influence the electronic and optical properties of silicon nano-crystals [9–11]. In these nanomaterials, most of Si atoms are positioned on or near the surface and are presumably affected by the surface effects or passivation, and this could conduct to a substantial modification of their electronic structures. Albeit many models have been suggested to elucidate the source of PL in porous Si (exposed to air), until now its origin still remains controversial. According to the experimental evidence, it is still arduous to detect the surface effects from the bulk ones and to realize the size dependence on PL energies and radiative lifetimes in passivated Si nano-crystals. Thus, it is viable that the luminescence properties can be associated to the surface terminations with H atoms in Si-QDs. In the experimental realizations, Si QDs with ultra-small 1–2 nm-diameters seem to face obstacles [11,12], while density functional theory (DFT) simulations are thriving in predicting or corroborating the electronic structure of these systems. In this respect, our aim is to investigate the quantum confinement effects, the control of the electronic and optical properties that depend on the dot-size and surface passivation effects of Si-QDs. Several issues such as the hydrogen covered Si QDs and size dependence on the density of states and absorption spectra are still under the challenges. Hence, to clearly identify how the surface terminated by hydrogen atoms can affect the electronic and optical properties of host silicon QDs, we perform a theoretical analysis for these nanostructures with diameter up to 1.1 nm. Our simulations are based on first-principles method within the framework of pseudopotential scheme [14]. With this motivation, we focus particularly on the role played by hydrogen terminated silicon surface in eliminating the dangling bond effects. In order to elucidate theoretically the size effect on the electronic structure of Si QDs passivated by H-atoms and the behavior of detected red-shifts in PL, we modeled Si nanostructures with small and medium quantum dots. The dot-size dependence and hydrogen terminated surface effects on the energy gap and absorption spectra of Si dots are discussed. The results are compared with the available theoretical and experimental data.

In this paper, we investigate the effect of quantum confinement on the energy gap in both passivated and unpassivated silicon quantum dots with various sizes. In this respect, we are mainly interested to compute the density of states, optical absorption spectra and static dielectric constant as a function of dot-size and to examine the role of surface passivation by hydrogen. To gain new insight at the microscopic level of the bonding of unpassivated and H-passivated SiQDs, we calculate the distribution of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO). Hence, to discern these phenomena, it is relevant to analyze how the combination of hydrogen and size dot dependence affects the quantum confinement in these systems. The plan of the paper is as follows: In Section 2, we briefly discuss the computational method. In Section 3, we present our results and discussion. In Section 4 we conclude our main work.

## 2. Method of calculation

We have performed pseudo-potential ab-initio simulations [14] to investigate the effect of hydrogen atoms by passivating the surface of silicon QDs (the size variation from 0.2 to 1.1 nm) and the unsaturated Si QD's. DFT methodology presents a significant starting point in this kind of studies and can be employed for more complex materials to extract relevant microscopic information. In this work, the ab initio calculations are carried out by using pwscf package [14], while the basis set is a plane-wave pseudopotential scheme. The structural calculations are performed by employing DFT [15] with the standard generalized gradient approximation (GGA). In particular, we have used PBE exchange and correlation functional [16] and a plane-wave approach with the super cell method. For the exchange-correlation energy, we used ultrasoft Vanderbilt pseudopotentials with semicore corrections [17] for both Si and H atoms. The plane-wave kinetic energy cut-off is selected to be 45 Ry for ensuring the convergence of the total energy to be less than $10^{-5}$ Ry/cell. All the atoms are fully relaxed until the Hellmann–Feynman force acting on each atom is smaller than $10^{-4}$ Ry/a.u. The dots are then relaxed to minimize the total energy using the conjugate gradient algorithm [14].

Starting from a central Si atom, the Si nanoclusters are constructed by adding successively shells of Si atoms. Due to the limitation of computational resources, Si QDs with larger diameters are not considered in our study. For unsaturated Si QD's and Si QDs passivated by H-atoms, the nanoclusters with spherical shapes are represented by a large periodically repeated supercell ($20\sim$a.u.). With these configurations, the interactions between the dot and its replica are negligible. The spherical dots are modeled by generating the atomic positions at the bulk interatomic distances up to the maximum diameter. The H-terminated Si QDs possess tetrahedral clusters which are relaxed with an average of Si–Si and Si–H bond lengths of 2.36 Å and 1.45 Å, respectively. Stable configurations of all dots with given size are obtained by minimizing the total energy of each configuration. A ball and stick models for silicon quantum dots with various diameters are depicted in Fig. 1. The structures with hydrogen passivation are

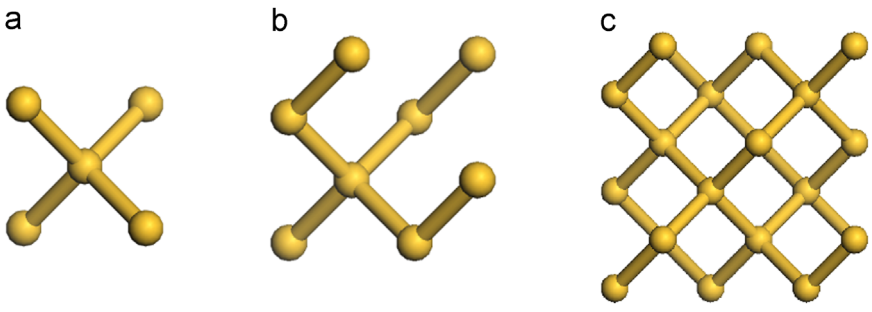


**Fig. 1.** Snapshots of various unsaturated Si quantum dots. Yellow dots are Si atoms. The size of these quantum dots is also given. (a) $Si_5$, (b) $Si_8$, and (c) $Si_{28}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)