Theoretical Investigation on Optical Characteristics of Functionalization Silicon Quantum Dots

M. E. Ahmed, J. P. Goss, R. J. Eyre, P. R. Briddon, M. A. Taylforth

School of Electrical, Electronic and Computer Engineering
Newcastle University, Newcastle upon Tyne, NE1 7RU
England, United, Kingdom
M.E.M.Ahmed@ncl.ac.uk

ABSTRACT

Functionalization of silicon surfaces at the nanoclusters size, is a crucial improvement that can give a great opportunity to use them in an enormous range of applications, including optical sensing, biological fluorescence imaging and optoelectronic devices. Using density functional theory calculations, light-absorption and luminescence processes are modelled at the quantum mechanical level. Optimized geometries and electronic structures of hydrogenated silicon quantum dots of $\sim$1 and 1.6 nm diameter attached to a diversity of chemical functional groups are investigated. In-depth characterization of their electronic structure and optical absorption shows that the impact upon the optical properties of the quantum dot depends strongly on the form of the functional group: in some important cases electron states are introduced into the band-gap leading to non-radiative recombination.

1 Introduction

Silicon quantum dots (Si-QDs) have been attracting great interest because of their exceptional optical properties. Bulk silicon, the foundation stone material in current microelectronics, is an inefficient light emitter due to its indirect electronic band-gap, which requires lattice vibrations (phonons) to balance electron momentum during inter-band transitions. Such three-particle (electron, photon and phonon) collisions have very low probability and the emission efficiency of bulk silicon at room temperature is very low [1].

In contrast, silicon nanostructures with size of the order of or less than the bulk exciton orbit (5 nm) exhibits strong photoluminescence (PL) at room temperature [2], [3].

Quantum confinement pointed as a key factor [4], [5] but, because up to around 50% of the atoms in such Si-QD are at the surface, the role of surface states, perhaps involving oxygen [6], [7], is likely to be important. Termination using hydrocarbon chains is an effective way of stabilizing the surface against oxidation [8]–[10]. Furthermore, functionalization of Si-QDs with different chemically active molecules is currently being investigated for possible applications as luminescent labels in biological applications, since the intense luminescence of Si-QDs is at wavelengths where biological systems do not absorb strongly [11].

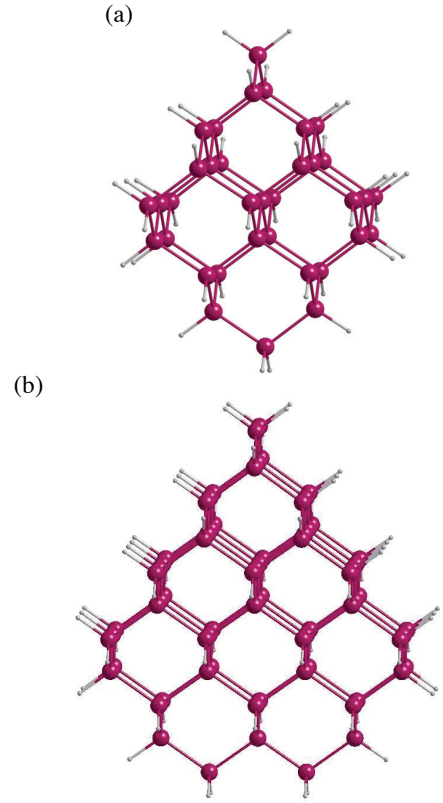

Figure 1: Schematics of the fully-hydrogenated Si-QDs used in this study : (a) $Si_{35}H_{36}$ and (b) $Si_{71}H_{60}$. Dark and light atoms are silicon and hydrogen, respectively.

2 Computational Method and Models

Calculations were carried out using the density functional technique, which is implemented in `AIMPRO` code (ab initio modelling program) [12]–[14]. All calculations presented here use the generalized gradient approximation [15] for total energies and forces, and core electrons are treated using norm-conserving pseudo potentials [16].

The valence wave functions are represented by independent sets of s and p Cartesian Gaussian orbitals of different four widths [17], with the addition of d-type Gaussians to allow for polarization in all cases other than for hydrogen. The quality of all basis sets is tested against a representative state (bulk silicon, silane, methane, CO, CF_4, CCl_4, CBr_4, ammo-

NSTI-Nanotech 2010, www.nsti.org, ISBN 978-1-4398-3402-2 Vol. 2, 2010

nia, phosphane, H_2S and iron metal) and the chosen basis sets reproduce experimental parameters for these systems to within a few percent. Matrix elements of the Hamiltonian are determined using a plane wave expansion of the density and Kohn-Sham potential [18] with a cutoff of 350 Ry, yielding well converged total energies with respect to the charge density basis. Optical absorption spectra are obtained from the calculated complex dielectric function [19], where the transitions between occupied and unoccupied states are subject to a polynomial broadening of width 0.1 eV.

The Si-QDs are modeled starting from tetrahedral, Si-atom centered, hydrogen-terminated clusters, $Si_{35}H_{36}$, and $Si_{71}H_{60}$, which are illustrated in Fig. 1. They have diameters of approximately 1.0 and 1.6 nm respectively.

The two H-terminated silicon quantum dots are used as a structural basis for our functionalized systems. Each non-functionalized, tetrahedral cluster was first structurally relaxed, yielding average Si–Si and Si–H bond lengths of 2.37 and 1.50 Å, respectively, both with standard deviations of 0.05 Å. Therefore, even at a relatively small size, the silicon in the Si-QDs is geometrically similar to bulk silicon.

For each functional group, one of the surface hydrogen atoms of the Si-QD is substituted by a linear alkane chain. The functional groups are located at the other end of the alkane chain. In all cases there are four methylene units (CH_2) between the "functional group" and the Si-QD, so that the functionalized systems can be characterized as (SiQD)–$(CH_2)_4$–R. The functional groups explored in this study are listed in Table 1).

3 Results

As a first approximation to the impact upon the optical properties of the functionalized alkane chains, we can examine the electronic spectra as represented by the Kohn-Sham levels of the molecular group and the hydrogen-terminated Si-QD, Table 1. We particularly focus upon the energies of their HOMOs and LUMOs, since we are looking for functional groups that introduce any states into the band-gap of the Si-QD. In these cases, the gap-states will in general contribute both to optical absorption and emission processes.

The simplest, and commonly employed example is the bare alkane functional group. Table 1 lists the HOMO and LUMO energies for the two cluster sizes. The HOMOs of the alkane chain is at -7.59 eV, far below the HOMO of even the smallest Si-QD which we locate at -6.03 eV. Similarly, the LUMO of the alkane chains are at 0.83 eV , far above the LUMO of the smallest Si-QD which lies at -2.39 eV. Since the HOMOs and LUMOs of Si-QDs increase and decrease monotonically with increasing size, the alkane chains, when separated from the Si-QDs, are not expected to introduce any molecular orbitals in the gap of the dots. This is confirmed in the electronic spectra of the alkane functionalized Si-QDs, which have HOMOs and LUMOs with no significant difference in energy from the undecorated cases. Thus, as has been previously concluded [20], we find that the functionalization

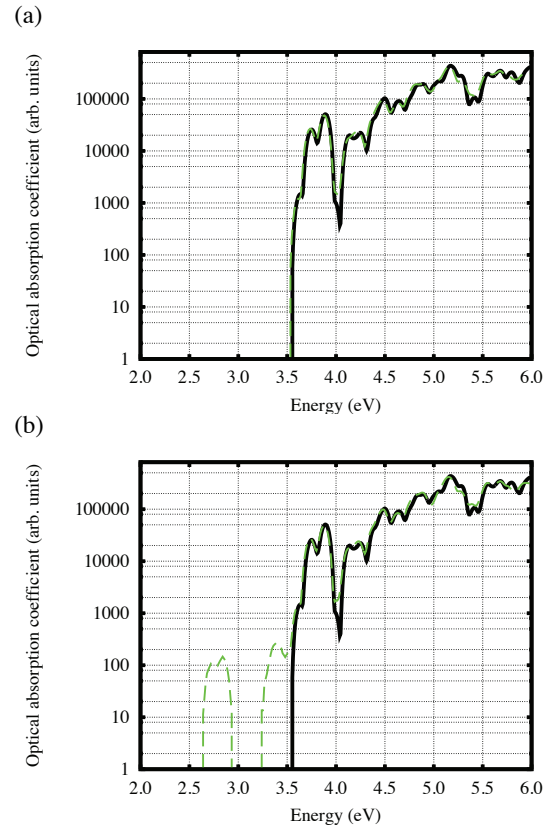

Figure 2: Plots of the charge density associated with the (a) HOMO and (b) LUMO. These two states of aldehyde functional group for chain of four carbon atoms length C_4H_8 attached to the 1 nm Si-QD, represent gap states relative to undecorated fully-hydrogenated silicon dot.

with simple alkanes has no significant impact upon the electronic structure in the vicinity of band-gap.

In addition, Fig. 2(a) shows the calculated optical absorption for the alkane functionalized 1 nm Si-QD in comparison to the undecorated Si-QD. There is no significant difference in the region of interest, consistent with the absence of any gap-states in the electronic structure.

Indeed, this general picture is also found for a range of common functional groups. From Table 1 we can say that alkene, alcohol, acid-chloride, nitrile, bromide, chloride and fluoride all yield HOMOs below the HOMOs of the two Si-QDs in this study, so do not introduce any occupied molecular orbitals into the Si-QD band-gap. Similar examination of the relative energies of the LUOMOs shows that we do not expect any empty states to be present either. This is confirmed by examination of the electronic structure and optical absorption spectra of the composite systems.

As an example of groups generating gap-states, Table 1 showes numerical results for aldehyde. Here, a new state localized on the functional group lies *well above* the HOMO of the 1 nm Si-QD. The localization of the HOMO and LUMO

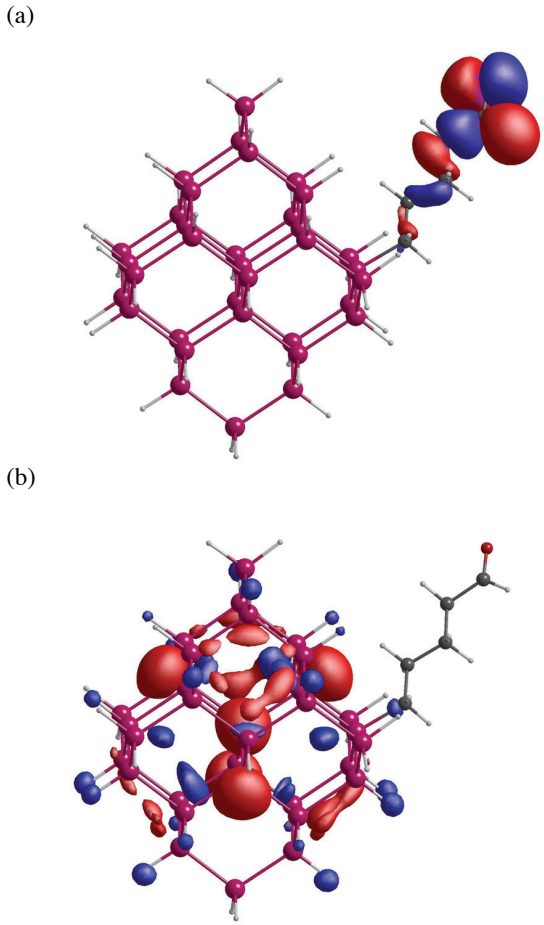

Figure 3: Plots of the charge density associated with the (a) HOMO and (b) LUMO of the. These two states of aldehyde functional group for chain of four carbon atoms length C_4H_8 attached to the 1 nm Si-QD, represent gap states relative to undecorated fully-hydrogenated silicon dot.

are illustrated in Fig. 3. The fact that the HOMO and LUMO are localized in different parts of the system means that the probability of a photon being absorbed by the promotion of an electron on the aldehyde group to the empty states of the Si-QD, is small, since this probability depends sensitively upon the overlap of the molecular orbitals. Figure 2(b) shows that in the 1 nm case, the gap state lowers the energy of onset of optical absorption by about 1 eV, but the magnitude is very low in comparison to that associated with the Si-QD.

We note that the aldehyde related gap state remains around the same energy in the composite systems, independent of the Si-QD size (Table 1). Therefore, as the Si-QD HOMO increases in energy with increasing Si-QD radius, it approaches that of the aldehyde group. This variation with cluster size is also captured in the optical absorption, as plotted in Fig. 4. The relatively small amount of sub-gap optical absorption merges into that arising from the Si-QD as the core diameter increases.

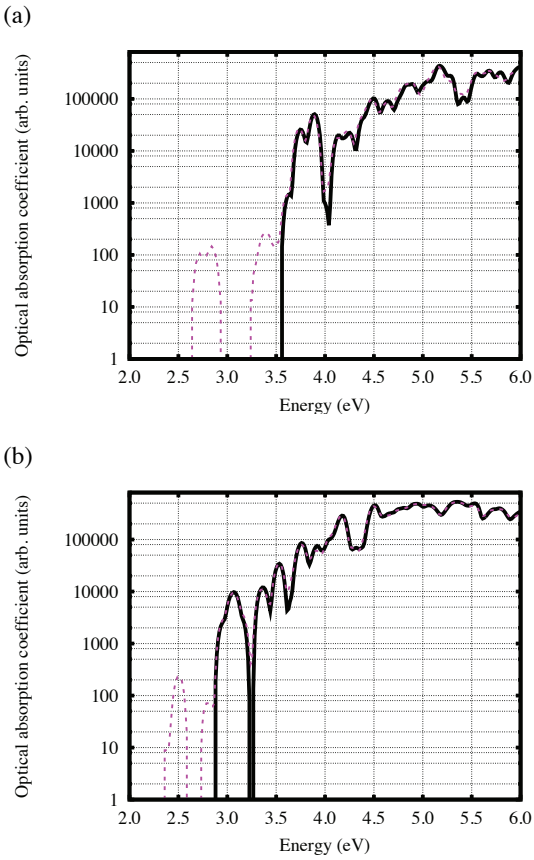

Figure 4: Plot of the calculated optical absorption spectra for aldehyde functionalized Si-QDs. In each case the black solid line is the optical absorption coefficients for undecorated Si-QD, purple dashed line is Si-QD–$(CH_2)_4$–aldehyde, respectively. (a) $Si_{35}H_{36}$–$(CH_2)_4$–aldehyde and (b) $Si_{71}H_{60}$–$(CH_2)_4$–aldehyde.

A summary of the numerical results obtained for the range of functional groups examined may be found in Table 1. Alkene and aldehyde groups constitute examples of two of the classifications we divide out results into, the former being groups which leave the band-gap unaffected, and the latter being an example that introduces gap-states. In some cases, however, it is less clear. For example arene functional groups only very slightly affect the electronic structure in the vicinity of the band-gap, but by examining the localisation of the HOMO in these cases it is clear that the pathology is closer to aldehyde than to alkene.

4 Conclusions

In conclusion, we have performed density-functional calculations examining the of process of functionalized of hydrogenated silicon quantum dots of about 1.0 and 1.6 nm in diameter, which have been attached to a range of functional groups.

Table 1: Electronic structure data for 1.0 and 1.6 nm Si-QDs and functional group linking via C_4H_8. HOMO and LUMO energies are in eV and relative to the vacuum level at zero. The groups are ranked by increasing energy of the HOMO of the H-$(CH_2)_4$-R system, and divided in columns by the size of the Si-QD.

	$Si_{35}H_{36}$		$Si_{71}H_{60}$	
Family Name	E_H	E_L	E_H	E_L
Pure QD	-6.03	-2.39	-5.68	-2.72
Acid-Cl	-6.06	-2.44	-5.70	-2.75
Nitrile	-6.10	-2.49	-5.75	-2.81
Chloride	-6.04	-2.43	-5.70	-2.76
Bromide	-6.03	-2.42	-5.69	-2.75
Fluoride	-6.03	-2.42	-5.69	-2.75
Alcohol	-5.99	-2.38	-5.65	-2.71
Alkene	-5.98	-2.37	-5.65	-2.71
Alkane	-5.97	-2.36	-5.65	-2.71
Alkyne	-5.78	-2.38	-5.66	-2.72
Arene	-5.66	-2.37	-5.65	-2.71
Carboxylic-acid	-5.62	-2.38	-5.63	-2.72
Amide	-5.51	-2.40	-5.47	-2.70
Thiol	-5.50	-2.41	-5.51	-2.74
Amine	-5.44	-2.37	-5.47	-2.73
Aldehyde	-5.11	-2.39	-5.16	-2.75
Sulfide	-5.02	-2.40	-5.01	-2.71

However, we note two things. First, as the size of the Si-QD increases, the HOMO of the undecorated Si-QDs moves up in energy, and for many of the functional groups the gap states present in the 1 nm Si-QD case dropped below the valence band top in case of 1.6 nm Si-QD. Moreover investigates are on-going into the role of increasing the chain length upon the electronic and optical properties of Si-QDs.

Secondly, in practice there is usually some oxide present in the surface of the Si-QD and although there is no reason to expect a qualitative change to our conclusions, the relative position of the Si-QD HOMO and the function group states may well be affected. Similarly, the solvent in which functionalised Si-QD systems are typically suspended has also not yet be considered, and the electrostatic interactions between functional groups and solvent molecules would also impact upon the location of the gap states. Studies are on-going into the role of surface oxide.

In addition, in some cases the excited states are expected undergo some structural relaxation associated with the population of some bonding orbital, such as in the case of alkenes where the molecular HOMO is close in energy to the Si-QD HOMO. A direct simulation of the excited states in order to develop a more quantitative picture for the optical emission is under development.

REFERENCES

[1] J. I. Pankove, *Optical Processes in Semiconductors* (Dover Publications, New York, 1971).

[2] J. Choi, N. S. Wang, and V. Reipa, Langmuir **25**, 7097 (2009).

[3] P. R. Coxon, Y. Chao, B. R. Horrocks, M. Gass, U. Bangert, and L. Siller, J. Appl. Phys. **104**, 084318 (2008).

[4] V. Lehmann and U. Gijsele, Appl. Phys. Lett. **58**, 856 (1991).

[5] D. König, J. Rudd, G. Conibeer, and M. A. Green, Mater. Sci. Eng. B **159–160**, 117 (2009).

[6] M. V. Wolkin, J. Jorne, P.M. Fauchet, G. Allan, and C. Delerue, Phys. Rev. Lett. **82**, 197 (1999).

[7] R. J. Eyre, J. P. Goss, R. M. MacLeod, and P. R. Briddon, Phys. Chem. Chem. Phys. **10**, 4495 (2008).

[8] F. M. Dickinson, T. A. Alsop, N. Al-Sharif, H. K. Berger, C. E. M.and Datta, L. Siller, Y. Chao, E. M. Tuite, A. Houltona, and Horrocks B. R., Analyst **133**, 1573 (2008).

[9] J. Choi, S. Tung, N. S. Wang, and V. Reipa, Nanotechnol. **19**, 085715 (2008).

[10] L. Mangolini1, D. Jurbergs, E. Rogojina, and U. Kortshagen, Phys. Status Solidi C **11**, 3975 (2006).

[11] X. Michalet, F. F. Pinaud, J. M. Bentolila, L. A.and Tsay, S. Doose, G. Li, J. J.and Sundaresan, A. M. Wu, S. S. Gambhir, and S. Weiss, Science **307**, 538 (2005).

[12] R. Jones and P. R. Briddon, in *Identification of Defects in Semiconductors*, Vol. 51A of *Semiconductors and Semimetals*, edited by M. Stavola (Academic Press, Boston, 1998), Chap. 6.

[13] P. R. Briddon and R. Jones, Phys. Status Solidi B **217**, 131 (2000).

[14] M. J. Rayson and P. R. Briddon, Computer Phys. Comm. **178**, 128 (2008).

[15] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[16] C. Hartwigsen, S. Goedecker, and J. Hutter, Phys. Rev. B **58**, 3641 (1998).

[17] J. P. Goss, M. J. Shaw, and P. R. Briddon, in *Theory of Defects in Semiconductors*, Vol. 104 of *Topics in Applied Physics*, edited by David A. Drabold and Stefan K. Estreicher (Springer, Berlin/Heidelberg, 2007), pp. 69–94.

[18] M. J. Rayson and P. R. Briddon, Phys. Rev. B **80**, 205104 (2009).

[19] C. J. Fall, A. T. Blumenau, R. Jones, P. R. Briddon, T. Frauenheim, A. Gutiérrez-Sosa, U. Bangert, A. E. Mora, J. W. Steeds, and J. E. Butler, Phys. Rev. B **65**, 205206 (2002).

[20] D. König, J. Rudd, M. A. Green, and G. Conibeer, Phys. Rev. B **78**, 035339 (2008).