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The electronic and optical properties of silicon nanoclusters: absorption and emission

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Abstract

The electronic and optical properties of silicon nanocrystals passivated with hydrogen and oxygen have been investigated both in the ground- and in an excited-state configuration, through different ab-initio techniques. The presence of an electron–hole pair leads to a strong interplay between the structural and optical properties of the system. The structural distortion of the nanocrystals induced by an electronic excitation is analysed together with the role of the symmetry constraint during the relaxation. The structural distortion can account for the experimentally observed Stokes Shift. Size-related aspects are also analysed and discussed.
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1. Introduction

Efficient, visible light emission from porous silicon [1] as well as optical gain recently observed in silicon nanocrystals [2,3] have claimed a lot of interest because of the promising application in optical nanodevices [4].

Understanding and controlling the properties of these novel materials requires to learn more about the physical mechanisms at the origin of these phenomena, and this implies the analysis of both the ground and excited state of the optically active nanodots.

The theoretical investigation of phenomena such as the Stokes shift, the photoluminescence emission energy vs nanocrystals size, etc., can give a fundamental contri-

bution to the understanding of how to tune the optical response of such systems.

A lot of work has been done dealing with excited nanoclusters, but a clear comprehension of some aspects is still lacking. Furthermore recent experimental data have shown a strong evidence that the surface changes of silicon nanocrystals exposed to oxygen produce substantial impact on their optoelectronic properties, thus oxidation at the surface has to be taken into account.

In this paper we present a detailed analysis of hydrogenated silicon nanocrystals and some preliminary results of oxygenated ones. The aim is the systematic investigation of their structural, electronic and optical properties as a function of size and symmetry, as well as pointing out the main changes induced by the nanocrystal electronic excitation.

The optical response can be understood only if related to the changing of both the electronic spectrum

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and the structural re-arrangement of atoms following up the excitation.

The investigation of excited nanocrystals from first-principle calculations can be done within several schemes. Many controversial points, relative to the range of applicability of such methods as well as the meaning of their respective results, still exist [5–10].

Here we show the results of a pair-excitation energy calculation [9–11]. Within such a model, the absorption/emission path is schematised as a four-level process which can be described as follows.

The effect of the excitation is to change the ground-state levels occupation, by promoting one or more electrons to unoccupied states. Therefore we have to distinguish between the ground-state level occupation and the excited-state one, where an electron–hole (e–h) pair is created by, e.g., excitation of one electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), thus leaving a hole in the HOMO.

It is crucial to note that once the e–h pair has been excited the charge density distribution changes, thus perturbing the forces acting on the atoms. The ions follow the excitation relaxing to a new equilibrium geometry, provided that the time taken by this process is shorter than the e–h pair recombination time. Therefore, the excitation and de-excitation processes involve two atomic configurations, which will be referred to as ground-state and excited-state geometries. This gives rise to four possible electronic/atomic configurations with their corresponding total energies, as follows:

(i) ground state as the starting point, whose total energy is E_1,
(ii) one e–h pair induced by the excitation, described by the excited-state level occupation but in the ground-state geometry, whose total energy is E_2,
(iii) cluster relaxation in the presence of the e–h pair, toward the excited-state minimum energy geometry, whose total energy is E_3,
(iv) e–h pair recombination, ground-state occupation, excited-state geometry, total energy E_4.

After (iv) the system can eventually relax toward the starting, ground-state geometry. We are going to show that the excitation can induce significant changes on the electronic and structural properties of the system and, mostly, that there is a strong interplay between the electronic levels occupation and the cluster geometry.

The total energy calculations have been done in the framework of the density functional theory (DFT) using the ABINIT code (plane waves basis set, norm-conserving Hamann-type pseudopotentials) [12]. Gradient-corrected Perdew–Burke–Ernzerhof (GGA-PBE) exchange-correlation functional has been used. Each nanocrystal has been embedded within a large supercell

(13.4–16.9 Å, according to the cluster dimension) and the energy cut-off for plane waves chosen to be 32 Ry for the hydrogenated clusters and 60 Ry for the oxidized ones.

The GGA-PBE results for the HOMO–LUMO energy gap have then been compared, in some cases, with those obtained within LDA in the independent particle random phase approximation (IPRPA) in which the local field has been or not included in the calculation [13,14] and with GW calculations.

The considered hydrogenated nanocrystals are SiH_4, Si_5H_{12}, $Si_{10}H_{16}$, $Si_{29}H_{36}$ and $Si_{35}H_{36}$ and for the oxygenated ones the $Si_{10}H_{14}O$-double bonded, $Si_{10}H_{14}O$-bridge bonded, $Si_{10}H_{16}O$-bridge bonded, $Si_{29}H_{34}O$-double bonded and finally the $Si_{29}H_{34}O$-bridge bonded.

For each of these clusters we have studied both the ground- and the excited-state electronic occupation and determined the four energy-levels E_1, E_2, E_3 and E_4 defined above.

The absorption edge can be defined as $E_{abs} = E_2 - E_1$ and the emission peak as $E_{em} = E_3 - E_4$. It is worth noting that following this scheme we calculate both energies from total energy differences, thus (at least partially) overcoming well-known problems of DFT with HOMO–LUMO gaps (that is, excitation energies calculated from Kohn–Sham levels which systematically underestimates the energy gaps). Moreover, in this way we properly take into-account the Coulomb interaction between the hole and the electron.

Because within this model absorption and emission occur at different nanocluster geometries, the corresponding energies will be, in general, different. Therefore, this also gives a possible explanation for the Stokes shift (or, at least, of the contribution to it arising from excitation-induced relaxation). It is also clear that a strong interplay between the electronic and structural properties takes place, namely structural changes induce energy levels rearrangement and vice versa [15].

It is worth mentioning that recent results concerning optical gain in silicon nanocrystals have been described within a four-level, rate-equation model [3,16]. The nature of such levels can be interpreted within the scheme depicted above.

2. Results on hydrogenated clusters

In Fig. 1 the calculated relaxed geometries for the considered clusters in both the ground- and excited-state configurations are shown. The T_d symmetry of the clusters is broken under excitation, resulting in a significant distortion of the smaller clusters.

Photodissociation of silanes and polysilanes is confirmed in many experimental works [17].

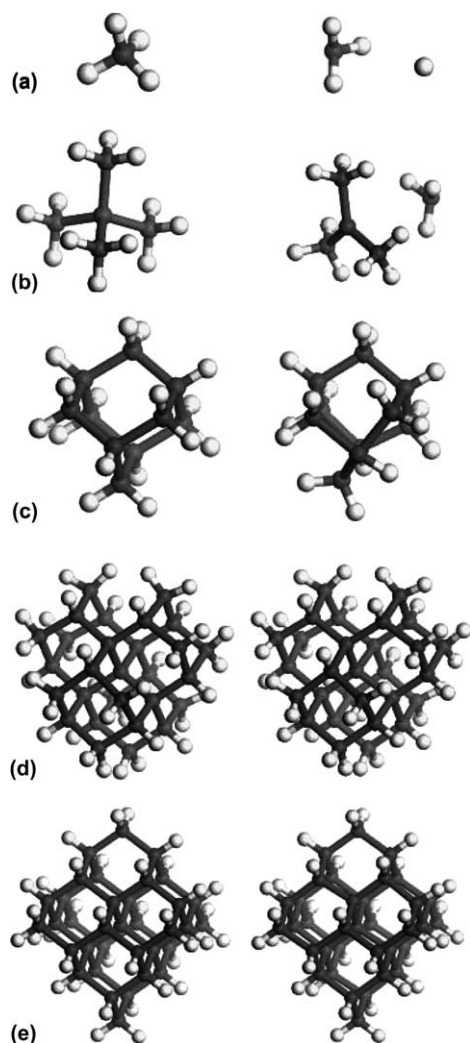Nevertheless we have verified that, starting from the distorted excited state geometry and going back down

Fig. 1. Relaxed structures for the (a) SiH_4, (b) Si_5H_{12}, (c) $Si_{10}H_{16}$, (d) $Si_{29}H_{36}$ and (e) $Si_{35}H_{36}$ clusters in both the ground- (left) and excited-(right) state configuration.

to the ground state, the systems relax again to the T_d symmetric configuration.

We point out that if the optimisation is performed imposing the symmetry constraint it is possible to fall into local minima. In order to clearly show this point two different calculations for the excited state configura-
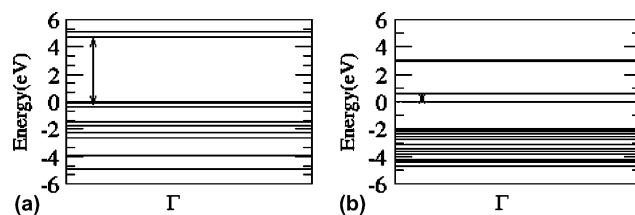

Fig. 2. Calculated energy levels for the $Si_{10}H_{16}$ in the excited state configuration relaxed (a) with T_d symmetry constraint and (b) without T_d symmetry.

tion both keeping and breaking the T_d symmetry of the ground state have been carried out. It is interesting to observe that the atomic positions of both the ground and excited states for a cluster with T_d symmetry are almost the same, whereas this does not occur if we do not impose any constraint during the relaxation.

Similarly, the calculated Kohn-Sham levels obtained for the excited states are very close to those obtained for the ground-state when the symmetry constraint is not relaxed as it is shown in the Fig. 2a and b for the $Si_{10}H_{16}$. A similar result is obtained for the HOMO and LUMO square modulus contour plots calculated for the cluster in the excited state electronic configuration, shown in Fig. 3a (T_d symmetry) and b (no symmetry).

We can conclude that both the energy levels and the resulting charge distribution for the T_d excited cluster practically do not change with respect to the ground state.

These findings show how the electronic and geometrical properties obtained by keeping the symmetry constraint for the excited state calculation are very far from those we obtained at the actual energy minimum and lead to a wrong geometry and charge density of the excited state.

The analysis of the HOMO and LUMO wave functions shows that they are strongly localized in correspondence of the distortion, giving rise to defect-like states which reduce the gap. Such a reduction can be clearly seen in Fig. 2b, where the energy levels for the $Si_{10}H_{16}$ cluster are shown. The HOMO–LUMO levels in the ground- and excited-state configuration provide a possible interpretation of the nature of the four levels
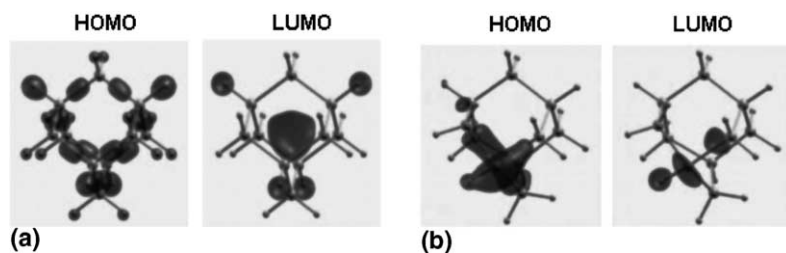

Fig. 3. HOMO and LUMO square modulus contour plots calculated for the $Si_{10}H_{16}$ cluster in the excited state configuration relaxed (a) with T_d symmetry constraint and (b) without T_d symmetry.

invoked for explaining optical gain in silicon nanocrystals [3,16].

The analysis of the ground-state geometries shows that the average Si–Si bond length is an increasing function of the size resulting in an increase of the cluster density with respect to bulk Si. On increasing the number of atoms within the cluster, it is found that bulk Si structural properties are retrieved. No clear trend can be instead identified for the excited-state geometries.

The structural properties are immediately reflected into the electronic spectrum of the system, shown in Fig. 4. The absorption (upper curves) and emission (lower curves) energies as a function of the number of atoms in the cluster calculated from both pair-excitation energies (circles, corresponding to $E_{abs} = E_2 - E_1$ and $E_{em} = E_3 - E_4$ respectively) and HOMO–LUMO gaps (squares) are reported. The well known reduction of the absorption gap with the size clearly comes out. Moreover, it is evident that the relaxation in presence of the e–h pair significantly modifies such a gap, explaining why emission occurs at lower energies than absorption (Stokes shift).

In Fig. 5 we show the Stokes shift, obtained as absorption–emission peaks difference $E_{abs} - E_{em}$. It is seen that it is a decreasing function of the size. At least the structural contribution considered here, which is a consequence of the different geometries in the ground- and excited-state configurations, is expected to have this behaviour, because for very large sizes the structural change induced by the excitation only slightly perturbs the equilibrium ground-state bonds and angles.

A good agreement between the GGA-PBE and LDA HOMO–LUMO gaps (obtained with two different ab-initio approaches [13,14]) for all the clusters studied has been found. In the case of SiH$_4$ and Si$_5$H$_{12}$, we have also performed a further, preliminary analysis of the excited states properties. We have calculated the GW cor-

Fig. 5. Stokes shift calculated from pair-excitation energies as a function of the number of Si atoms within the cluster.

rections [18] to the DFT gap [14], thus obtaining the 'electronic gap'. This gap is, as expected, much larger than the optical one, since excitonic effects are not included. In order to estimate the excitonic effects, we have also performed a TDLDA and LDA-IPRPA calculation for the optical spectra, with local fields effects included. The resulting optical gaps are listed in Table 1. The agreement with optical experiments is, for Si$_5$H$_{12}$, remarkably good, while more tests are needed for Si$_1$H$_4$. We plan to perform, for this system, a full excitonic calculation by solving the Bethe–Salpeter equation.

A substantial agreement has also been observed from the comparison of our results with both previous DFT ground state and Stokes shift calculations (for details see Ref. [15]).

3. Results on partially oxidized clusters

We present preliminary results on partially oxidized clusters, studying the effects of different Si/O bonds at the surface.

Two classes of systems have been studied, based on the Si$_{10}$ and the Si$_{29}$ core based nanoclusters, and considering three type of Si/O bonds: the Si–O–Si back
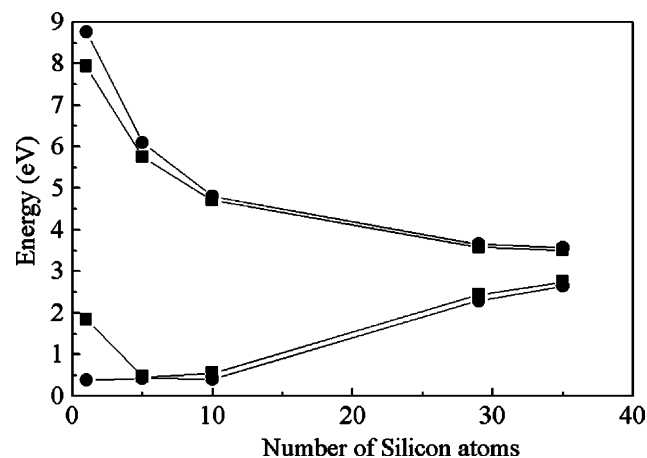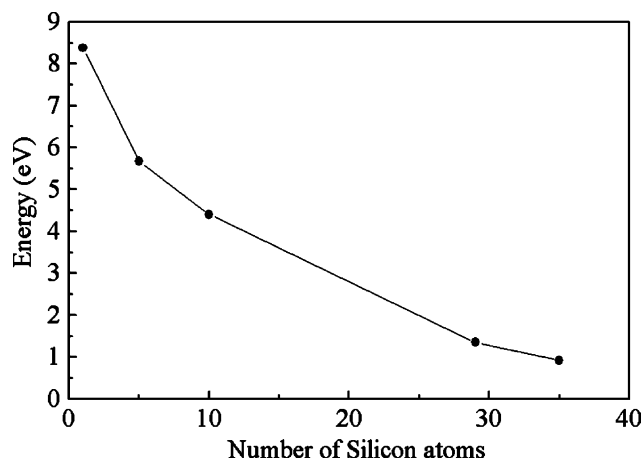

Fig. 4. Absorption (upper curves) and emission (lower curves) calculated from both pair-excitation energies (circles) and HOMO–LUMO gaps (squares).

Table 1
Calculated vs experimental values for the electronic and optical gap of SiH$_4$, Si$_5$H$_{12}$ and Si$_{10}$H$_{16}$ clusters

	Si$_1$H$_4$	Si$_5$H$_{12}$	Si$_{10}$H$_{16}$
PBE	7.93	5.75	4.71
LDA[13]	7.81		4.59
LDA[14]	7.91	5.77	
GW	12.3	9.6	
RPA + LF	7.8	6.5	
TDLDA	7.8	6.5	
EXP.	8.8	6.5	

bond, the Si–O–Si bridge and the Si=O double bond, whose geometries are shown in Fig. 6.

In Fig. 6 we also show the HOMO and LUMO charge density for the systems studied both in their ground and excited electronic configurations. The energy levels calculated for these clusters are shown in Fig. 7. The reduction of the gap in the excited electronic configuration is less evident for the case of the cluster with the double-bonded oxygen; the same can be observed for the double-bonded $Si_{29}H_{34}O$.

The different behavior for the double bonded clusters is also shown in the calculation of the Stokes shift, obtained as absorption–emission gaps difference $E_{abs} - E_{em}$ for the Si_{10} and the Si_{29} core based nanoclusters.

In the case of the $Si_{10}H_{14}O$ double-bonded we calculate a Stokes shift of 1.70 eV [$E_{abs} = 2.79$ eV, $E_{em} = 1.09$ eV] and for the $Si_{29}H_{34}O$ double-bonded we obtain 1.65 eV [$E_{abs} = 2.82$ eV, $E_{em} = 1.17$ eV]; instead for the $Si_{10}H_{14}O$ bridge-bonded the value is 3.90 eV [$E_{abs} = 4.03$ eV, $E_{em} = 0.13$ eV] while for the $Si_{29}H_{34}O$ bridge-bonded is 0.28 eV [$E_{abs} = 3.29$ eV, $E_{em} = 3.01$ eV].

The oxygen double-bonded seems hence almost size independent: actually, the presence of this kind of bond creates localized states within the gap that are not affected by quantum confinement as previously predicted by Luppi and Ossicini [19].

The agreement between GGA-PBE and LDA-IRPRA [13] calculation is good also for the oxidized clusters. In fact, regarding the HOMO–LUMO gap, we have obtained 2.48 eV, 3.83 eV and 4.15 eV for the $Si_{10}H_{14}O$ double-bonded, $Si_{10}H_{14}O$ bridge-bonded, and $Si_{10}H_{16}O$ back-bonded, respectively, in the GGA-PBE scheme to be compared with the IPRPA outcomes of 2.47 eV,

3.74 eV, and 4.00 eV for the same structures, although sometimes HOMO–LUMO transitions have very little oscillator strength, as in the case of $Si_{10}H_{16}O$ back-bonded.

It is interesting to note that when the dielectric response is calculated with the inclusion of the local field effects, the oscillator strengths are shifted significantly towards higher energies; actually the main absorption edges are obtained at 3.7 eV, 4.0 eV, and 5.2 eV, respectively, for the above cited structures.

4. Conclusions

The electronic and optical properties of hydrogenated and oxidized silicon nanoclusters have been investigated by pair-excitation energies calculations. The effect on the cluster geometry due to the excitation has been studied, showing a structural rearrangement of the atoms within the cluster and a modification of the electronic spectrum. This allows us to explain the difference between absorption and emission gaps, and hence the Stokes shift.

In the case of hydrogenated clusters the Stokes shift clearly depends on the cluster size; for oxidized clusters, instead, we have found that the double bonded oxygen, contrary to the bridging configurations, creates strongly localised states within the gap that induce size independent absorption and emission energies and consequently a size independent Stokes shift.

Finally, the inclusion of local field effects in the calculation leads to an overall shift of the oscillator strengths towards higher energies.
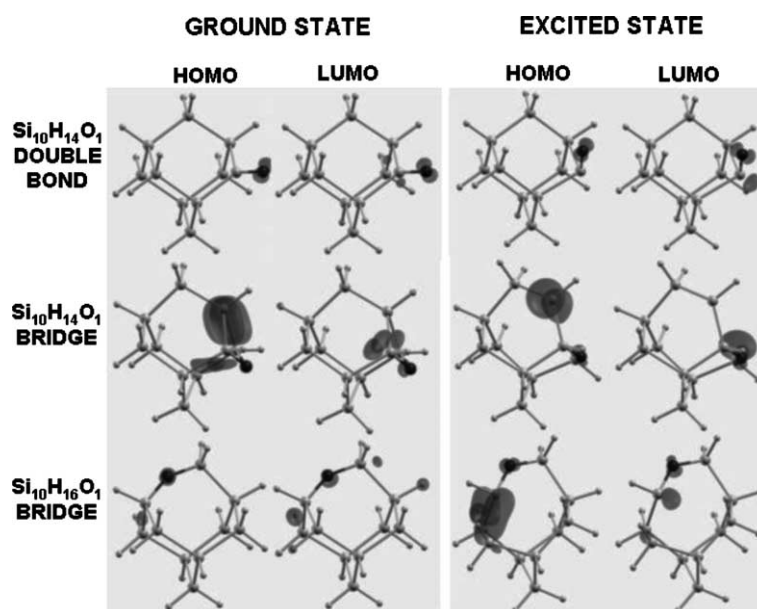

Fig. 6. Calculated HOMO and LUMO charge density for $Si_{10}H_{14}O$-double, $Si_{10}H_{14}O$-bridge and $Si_{10}H_{16}O$-bridge for the ground and excited states; the structures shown are the relaxed ones.
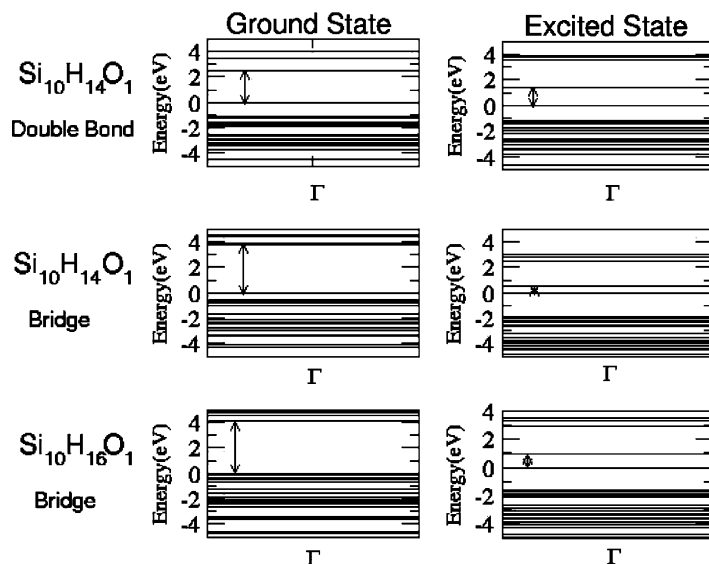
Fig. 7. Calculated energy levels for $Si_{10}H_{14}O$-double, $Si_{10}H_{14}O$-bridge and $Si_{10}H_{16}O$-bridge clusters in the ground and excited state configuration.

Acknowledgements

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