

OPTICAL PROPERTIES OF CLUSTERS

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In this paper, we discuss in detail the theoretical results obtained with using the local functional density method in parameteric approximation of silicon clusters. One of the main conclusions is that the comparison between theory and experiments shows the possibility of different radiative channels for the recombination in porous silicon.

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1. Introduction

Research into semiconductor clusters is focused on the properties of quantum dots (QD) – fragments of semiconductor (for example, Si) consisting of some to hundreds of atoms – with the bulk bonding geometry and with surface states eliminated by enclosure. QD exhibit strongly size-dependent optical and electrical properties [1-3]. Two peculiar characteristics of semiconductors influence the ways in which we think of an ideal semiconductor cluster, which is often called a QD. First, it is important to realize that in any material, substantial variation of fundamental electrical and optical properties with reduced size will be observed when the electronic energy level spacing exceeds the temperature. In semiconductors, this transition occurs for a given temperature at a relatively large size compared to metals, insulators, or molecular crystals.

The luminescence observed for por-Si raises an interesting problem related to the possibility of using Si in optoelectronics [2]. One likely explanation is *quantum confinement*, induced by the formation of nanocrystallites, whose effect is to break partially the optical selection rules and allow the material to luminesce.

The most striking property of semiconductor nanocrystals is the massive change in optical properties as a function of size. As size is reduced, the electronic excitations shift to higher energy, and the oscillator strength is concentrated into just a few transitions. These basic physical phenomena of *quantum confinement* arise as a result of changes in the density of electronic states and can be understood by considering the relation between position and momentum for free and confined particles. For a free particle, or a particle in the periodic potential of an extended solid, the energy and the crystal momentum can both be precisely defined, whereas the position cannot. For a localized particle, the energy may still be well defined, but the uncertainty in position decreases, so that momentum is no longer well defined.

For example, the kinetic stability of tetrasilatetrahydride (Si_4H_4), hexasilaprismane (Si_6H_6) and octasilacubane (Si_8H_8) depends strongly on the steric bulkiness of the substituents (matrix). The silyl-substituted Si_nY_m ($Y=t-Bu$) is stable in an inert atmosphere, but is oxidized in air to give colorless solids. The 1,1,2-trimethylpropyl-substituted Si_nY_m ($Y=CMe_2CHMe_2$) is very stable even in air and survives for two weeks in the solid state. The prismanes with Si and Ge skeletons are yellow to orange.

These prismanes have absorptions tailing into the visible region. So, Si_6H_6 has an absorption band with a maximum at 241 nm tailing to ca 500 nm. The absorption band of Ge_6Y_6 ($Y=2,6\text{-i-Pr}_2\text{C}_6\text{H}_3$) has a maximum at 261 nm, which is red-shifted compared to that of Ge_6Y_6 because of the higher-lying orbitals of the Ge-Ge bonds [4].

2. Calculations of quantum confinement effect

A number of calculations have been performed over the last few years, for quantum dots as well as for silicon clusters since both possibilities have been invoked for porous silicon. They essentially belong to four classes: effective mass approximation (EMA), empirical tight binding (ETB), empirical pseudopotential (EPS), and finally ab initio local density functional theory (LDFT). In Fig. 1 we give the predicted band gaps versus size as obtained from LDFT calculations compiled in [5] for hydrogen-terminated Si-clusters, wires and slabs.

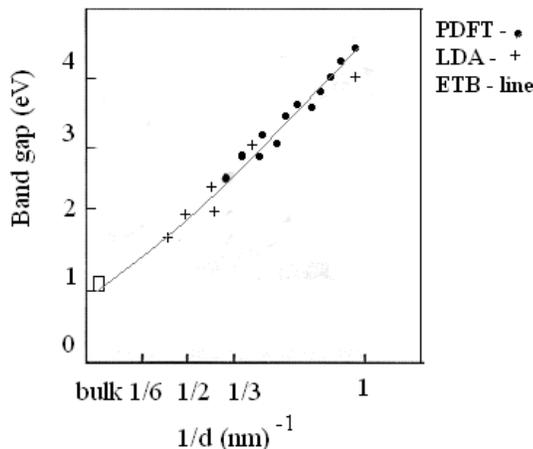


Fig. 1. Energy gap versus confinement parameter $1/d$ for hydrogen-terminated Si clusters ($d = a(0,75 N)^{1/3}$ for clusters, $d = a(0,75 N)^{1/2}$ for wires; $a = 0.54$ nm and N is the number of Si atoms in the unit cell).

They are compared to the results obtained in our group using DFT approach with parameters (PDFT [3]) providing an extremely good fit to the bulk band structure. One can notice a good agreement between the LDFT and PDFT predictions which gives some confidence into the reliability of these theoretical values. At this stage it is important to notice that the LDFT gap values include a rigid shift of 0,6 eV since it is known that LDFT underestimates the bulk band gap by this amount. Note that the theoretical calculation grossly overestimate the blueshift.

They must then be discarded since EMA can be considered as an approximation to the best ETB or EPS descriptions which match the effective masses. One can, however, wonder why parameterized techniques should provide quantitative estimates of the one-electron gap. The basic point is that they are based on the postulate of transferability of the parameters from the known bulk band structure (to which they are fitted) to the unknown crystallite case. If this is accepted, then an essential criterion by which a particular semi-empirical model can be judged is how well it describes the bulk band structure. So from Fig. 1 we could conclude that PDFT as well as corrected LDA techniques are likely to give reliable predictions for crystallites.

3. Channels for the radiative recombination

Fig. 2 presents a compilation of data showing that observed luminescence energies on porous silicon or silicon nanocrystals in an oxide matrix are consistently lower than the predicted optical gaps of Fig. 1. On the other hand, they qualitatively agree with optical

absorption data. Recent results also show that the luminescence of fresh porous silicon samples is subject to a large red shift when it is exposed to air and when the average size of the nanocrystals is smaller than 3 nm (Fig 3). On the other hand, recent luminescence measurements on silicon crystals obtained by silane decomposition are in good agreement with theory, but the luminescence is only observed for the largest crystallites. The situation is thus complex, even if it seems that the degree of oxidation of the samples plays an important role in the recombination mechanisms. All these results suggest that other channels for the radiative recombination are possible. Large Stokes shifts might be consistent with the eventual existence of deep luminescent centers. The problem is that nothing is presently known regarding the nature and origin of these states. Both from PDFT and LDA calculations such states indeed exist under the form of self-trapped excitons, most probably at the surface. A possible situation is the trapping of an exciton on a Si-Si bond of a surface dimer whose dangling bonds are saturated by hydrogen atoms. We have found another interesting situation with very small crystals, containing less than 50 silicon atoms, where we systematically obtain a large atomic relaxation in the excited state which induces an important reorganization of the bonds in the cluster. The consequence is a large Stokes shift between the absorption and the emission energies. Therefore, small nanocrystals could play a role in the luminescence of porous silicon.

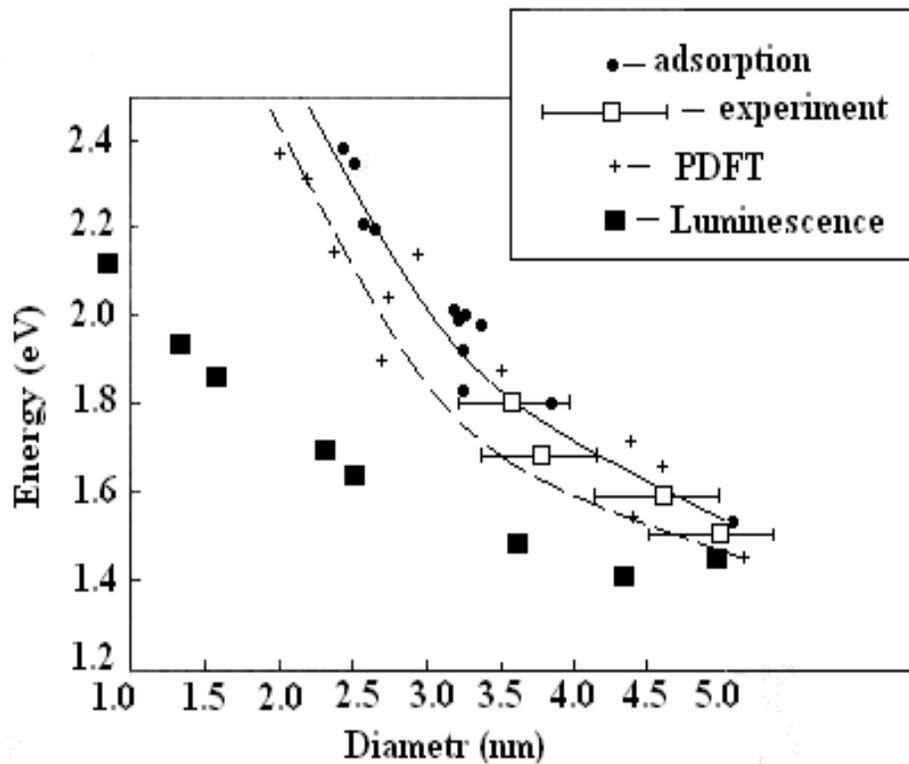


Fig. 2. Compilation of optical band gaps of silicon crystallites and porous silicon samples obtained from optical absorption and luminescence (filled symbols and also the more experimental results of B.Kohn group with error bars). Dashed and continuous lines: calculated values with and without the excitonic correction.

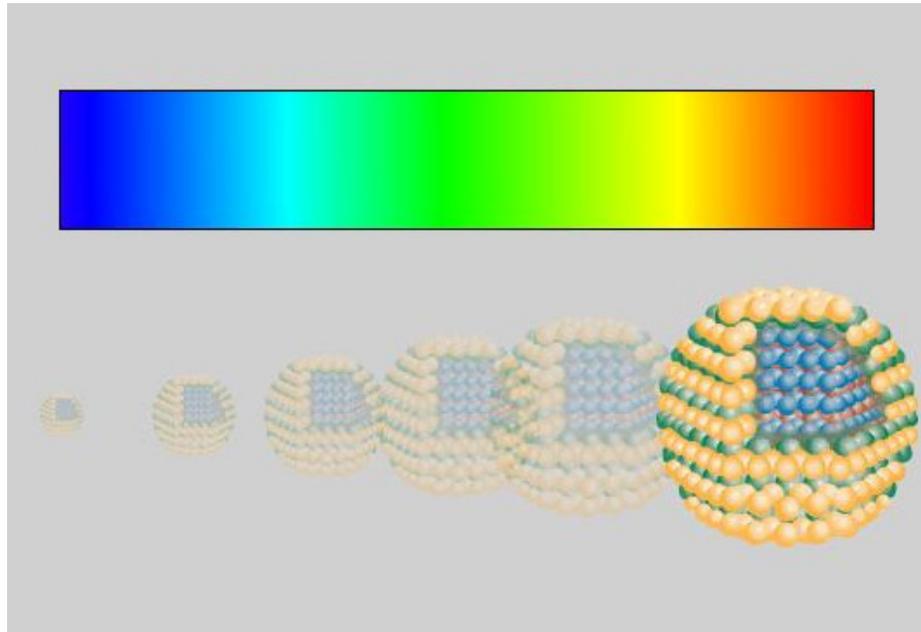


Fig. 3. Illustration of the large red shift for ball-like clusters.

We are presently investigating the possible existence of defect states in the band gap induced by the oxidation of the surface. Among different systems that we have studied, preliminary results show that an oxygen atom doubly bonded to a silicon atom ($\text{Si}=\text{O}$) at a nanocrystal surface is a good candidate to be involved in the luminescence of porous silicon. It gives rise to a deep level below the conduction band minimum which could explain the evolution with size of the luminescence peak in Fig. 3.

4. Structural dependence of the band gap

G. Allan with coworkers showed that the radiative recombination rate in spherical silicon nanocrystals (calculated as in Ref. [4]) was low and decreased for smaller band gap because of the indirect bulk band gap. In this regard, it would be of interest to use a direct gap phase of silicon such as Si-III (BC8) or to use materials like SiGe alloys or amorphous silicon because the disorder breaks the selection rules. But an essential question arises about the existence of quantum confinement effects in disordered materials. Here we describe recent results that we have obtained on these problems. The Si-III (BC-8) crystal phase is obtained for *t* bulk samples by releasing the pressure on the high-pressure *beta-tin* phase (Si-II) [5]. Existing theoretical calculations show that the valence band maximum and the conduction band minimum occur at the same H point in the Brillouin zone. BC-8 silicon is thus a direct gap material but the calculations conclude that it is close to a zero gap semiconductor. To calculate the electronic structure of BC-8 crystallites with size in the 1-3 nm range, we have chosen the same non-orthogonal ETB technique as used for silicon crystallites with the diamond structure but we have developed a specific parameterization for that structure.

Our results show that the confinement effect is quite similar for BC-8 and diamond clusters. The only difference when one goes from the BC-8 cluster to the diamond one with the same size comes from the bulk gap value which simply shifts the cluster gap energy. We have also performed PDFT calculations. One can see that the values

calculated with PDFT for two small clusters and shifted by 0.6 eV to take into account the underestimation of the bulk gap, are in very good agreement with our ETB calculation. This confirms the transfer-ability of the ETB parameters from the bulk material to clusters.

Experimentally, it was shown [2, 6, 7] that the BC-8 structure is obtained upon release of a high pressure on porous silicon. But the luminescence band remains practically unchanged except perhaps for a small shift (of order 0.1 – 0.2 eV) after release of the pressure. This finding completely disagrees with our predictions, where this redshift should amount to ~ 1 eV for crystallites of the same size. This would rule out quantum confinement as the origin of the observed luminescence band and favor other possibilities.

We compare the variation of the recombination rate as a function of the cluster gap for the BC-8 [5] and the diamond structures [8]. Because it has a direct bulk band gap, the recombination rate in the BC-8 phase remains constant and pretty high when the cluster size increases and the blue shift decreases. It is of the order of a few ms^{-1} (i.e. more than 10^3 times larger than in the diamond phase below 2 eV), but remains however lower than the result for GaAs ($\sim \text{ns}^{-1}$) which is also a direct gap semiconductor. However, the luminescence yield must be strongly improved for the BC-8 structure compared to the diamond structure.

With improved optical properties compared to silicon, $\text{Si}_x\text{Ge}_{1-x}$ alloys are also interesting materials. We have studied the strong confinement effects in SiGe clusters performing ETB calculations with the parameters. We consider spherical clusters passivated by hydrogen atom where the atomic sites are occupied randomly by Si or Ge atoms following the composition x . Our results shows that the band gaps of $\text{Si}_{0.8}\text{Ge}_{0.2}$ and Si clusters are quite close, with comparable blue-shift. This is due to the fact that the electronic states in bulk SiGe alloys are still delocalized, so they experience the full confinement effect as for crystalline Si (c-Si).

We now analyze the case of stronger disorder as obtained in amorphous silicon (a-Si). It raises extremely interesting problems related to the confinement induced blue shift of the energy gap: (a) does it exist in clusters of a-Si and is it comparable to what is obtained for c-Si; (b) what is the behavior of disorder-induced localized states in this regard. It has been often assumed that quantum confinements effects are small in a-Si nanostructures due to the short coherence length of free carriers in these materials. We will see that it is not true.

We calculate the electronic structure of a-Si and a-Si:H spherical clusters using the ETB and PDFT model. The interaction parameters are limited to first-nearest neighbors and the usual d^{-2} Harrison law can be used to calculate their variation with interatomic distance d . The starting structure for the a-Si or a-Si:H clusters is obtained by selecting the atoms belonging to the respective atoms unit cell. Due to the new boundary conditions the structure is no more in equilibrium and we have thus relaxed the atomic positions using a Keating potential.

A generally accepted picture of the electronic structure of a-Si is that it is still composed of valence and conduction bands separated by an energy gap but with bandtails of defect or disorder-induced localized states extending into the gap. For what follows we find it useful to classify the electronic states into three categories: delocalized states, experiencing the full confinement effect as for c-Si; strongly localized states with extension in space much smaller than the cluster diameter and energies deep in the gap, insensitive to the confinement effect and showing no blue shift; weakly localized states

with extension in space of the order of the cluster diameter and energies near the gap limits, subject to an intermediate blue shift.

5. Conclusion

To characterize the luminescence of our a-Si clusters with 1-2.5 nm size we have first computed their fundamental gap, i.e. the distance in energy between the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital). There is a substantial blue shift in both cases, more important for a-Si than for a-Si:H. Furthermore, our larger a-Si clusters give rise to a two-peak distribution. We have checked that the lower and upper peaks are, respectively, due to strongly and weakly localized or delocalized states. The relative intensity of the upper peak thus corresponds to the proportion of clusters which do not contain strongly localized states. The apparent blue shift in a-Si clusters has thus two origins: (a) the varying proportion of clusters with strongly localized states and (b) the normal confinement effect on the other states. This is confirmed on the sapie figure by the a-Si: H clusters which show only the second type of behavior.

Thus we have discussed in detail the theoretical calculations on the band gap of Si clusters. One of the main conclusions is that the comparison between theory and experiments shows the possibility of different radiative channels for the recombination in porous silicon which is a complex material.

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