

Optical Absorption of Small Hydrogenated Si Particles

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The visible luminescence in porous silicon has been interpreted as due to quantum confinement in nanostructures, either crystallites or wires. We study the structural and optical properties of small hydrogenated Si clusters, containing from 5 to 71 Si atoms, through an approach designed to treat consistently small molecules and bulk crystals: the Hartree-Fock method in the self-consistent Neglect of Differential Orbital (NDO) approximation. Specifically, we use the MNDO-AM1 hamiltonian (Modified NDO) when studying geometries, and the INDO hamiltonian (Intermediate NDO) for optical spectra. Both methods are thoroughly reparametrized for Si. We find that small clusters of ~ 50 Si atoms present vibrational properties already close to bulk Si. The whole optical absorption below 5 eV is associated with the “crystalline” silicon in the core of the cluster, showing evidence of quantum confinement effects; its energy range ($h\nu \sim 2.5 - 4.0$ eV) is too high to be directly associated to the optical emission of porous silicon.

I. Introduction

Both the optical absorption threshold and the room temperature visible luminescence in porous silicon show a large blue shift, as compared to bulk Si, which has been attributed to quantum confinement^[1,2]. Initial interpretations^[3-6] relating the luminescence to a Si-H amorphous phase or to surface structures involving O and H appear to be ruled out^[7-9]. In the debate on the dimensionality of the luminescent structures, crystallites seem to be favored over wires. Since a direct experimental measure of their size is not easily available, an indirect determination is obtained from their optical spectra and requires both theoretical and experimental information. Recent observations^[10] indicate that the luminescent structures may be considerably smaller than most of the estimates obtained from optical spectra.

Theoretical results relating the Si particle size to the energy of optical transitions^[11-16] show a very large spread (more than 100%). A certain degree of diffi-

culty is certainly expected when treating systems with a great number of atoms, in complex atomic configurations. Even so it is significant that such spread is found, and we believe that in this case a further difficulty may derive from the need of obtaining a *consistent trend* for the band gap of particles with very different size. As the electron localization changes drastically with size, correlation effects must be specifically investigated.

We present a study of the electronic structure and optical activity of small hydrogen-saturated Si clusters, through an approach which can treat both small molecules and bulk crystals; the chosen technique can incorporate the correlation effects that become critical at the small-cluster limit, and we may thus address the question of the size of the particles. We adopt the Hartree-Fock method in the semiempirical Neglect of Differential Overlap (NDO) approximations —successfully developed and used in quantum chemistry— to be able to treat self-consistently “large molecules” or the bulk crystal. When studying geome-

tries we adopt the MNDO-AM1 hamiltonian (Modified Neglect of Diatomic Overlap, Ref. 17), while for optical spectra we use the INDO hamiltonian (Intermediate NDO, Ref.18). Moreover, both methods are thoroughly reparametrized for Si, so as to describe accurately the sp^3 hybridization of tetrahedral environments. This is needed because such hybridization is generally not relevant in the systems used to obtain parameters for molecular chemistry. To do that, we developed^[19] a Bloch-periodic version of MNDO which was parametrized to yield bulk Si phonon frequencies (TO, LO and LA modes at Γ , X and L within 4% of the experimental values), while still reproducing the vibrational modes and frequencies of silane (SiH_4) and disilane (Si_2H_6). In the case of INDO we couple the Bloch-periodic model with a model for simulating nanocrystals (large clusters terminated with Si pseudoatoms^[20]), in order to introduce Configuration Interaction corrections: Parameters are obtained to reproduce the Si band-gap and valence-band features, with the same requirement that silane and disilane are well described. These parameters and the needed modifications to the hamiltonians constitute what we call NDO/Crystal, and are then used, here, in the usual molecular implementation for both methods.

A point worth recalling is that, for any method working within Hartree-Fock, eigenvalues of unoccupied one-electron-states or molecular orbitals (MO) have no physical meaning, so that the HOMO-LUMO (highest occupied – lowest unoccupied MO) eigenvalue difference in general cannot be taken to relate to a “gap energy” or optical transition. To obtain these energies correlation must be included: the first correction comes from calculating the total energy of a “pure” excited configuration. A pure excited configuration is associated with a Slater determinantal function, with a “hole” in the formerly occupied states and an “electron” in one of the formerly unoccupied states (single excitation), or two holes and two electrons, and so on. Full correlation can then be achieved if we allow Con-

figuration Interaction (CI) between the ground and all such excited configurations : a way of accounting for the need of electrons to avoid each other, which is not taken into account in simple Hartree-Fock. Clearly, CI correlation effects gain importance with confinement of the electrons. Therefore, a method that simulates the bulk crystal is not guaranteed to simulate small particles equally well, since the degree of localisation varies too much from one case to the other. This is why we are careful to check that both our methods reproduce also the properties of silane and disilane.

The techniques selected here are of course semiempirical, and use minimum basis sets. The parameters are chosen not to reproduce Hartree Fock results (we are using minimum basis) but experiment where it exists. The complexity of the problem has precluded the use of fully basis-converged, ab-initio techniques, be it within Hartree-Fock or Local Density formalisms^[16]. It is important however to note that we still incorporate the flexibility of correlation corrections, and so we can obtain corrected values for the excited configurations, pure or mixed.

To study small hydrogenated Si particles, we have chosen clusters in T_d (Γ -like) symmetry, centered either on a Si atom (clusters Si_5H_{12} , $\text{Si}_{17}\text{H}_{36}$, $\text{Si}_{29}\text{H}_{36}$, $\text{Si}_{35}\text{H}_{36}$, $\text{Si}_{71}\text{H}_{60}$) or on a T_d interstitial site ($\text{Si}_{10}\text{H}_{16}$); and bond-centered clusters in D_{3d} (X-like) symmetry ($\text{Si}_{26}\text{H}_{30}$, $\text{Si}_{44}\text{H}_{42}$).

The geometry for each cluster is obtained through MNDO/Crystal, allowing all atoms in the clusters to relax. We find that the topmost Si-like vibrations of the clusters fall within 1 meV of the bulk Si phonon frequencies already for clusters with as little as 29 Si atoms. This result may be relevant in view of the interpretation of phonon replica in photoluminescence experiments: Given the energy resolution of such experiments, an observed spacing typical of Si phonons is compatible with a cluster-based structure and sizes in the range studied here^[21].

Once we have the geometry, we calculate the

optical absorption spectra for the clusters through INDO/Crystal. Only for silane and disilane (“clusters” with 1 and 2 Si atoms) we allow full CI; for the larger clusters we build excitations with one-electron states lying within ~ 5 eV above or below the gap; we do not include two-electron excitations.

We come now to the main result of this work. In Fig. 1 we show the calculated energy gap for the hydrogenated Si clusters as a function of the number of Si atoms. We plot (a) the one-electron transition between the HOMO and LUMO of the ground electronic states, (b) the results including the “pure configuration” correlation correction, and (c) the results of the CI calculation.

We find that the first optical absorption involves an almost “pure” one-electron transition, for all investigated particles. The optical transitions originate in the “crystalline” silicon core of the cluster, and preserve the character of the bulk Si indirect gap transition, thus confirming the role of quantum confinement as generating the blue shift. Thus, for the transitions depicted in Fig. 1, we find that CI correlation is not important, which is a direct consequence of the almost pure character of the excited state (see below). This is not true for the higher-lying transitions. From Fig. 1 it is clear that for the smaller clusters the energy lowering associated with correlation *is not linear* in the number of Si atoms, since it depends, among other things, on the symmetry of the cluster and the specific transition involved.

The important result of Fig. 1 is the relation between particle size and energy gap. The average diameter of the larger Si structures studied here is of the order of 10 – 20 Å, and correspond to gaps in the region $\sim 2.5 - 3.5$ eV (the $\text{Si}_{35}\text{H}_{36}$ cluster with a 3.25 eV transition has an average diameter of ~ 11 Å). Extrapolation of these values to infinite diameter would yield a gap of ~ 1.5 eV, which indicates that, beside quantum confinement effects, also structural relaxations play a role in defining the gap of such small particles. Since

relaxation effects in the core of the particles must disappear after some critical size, it is not reasonable to extract from our results a range of diameters for particles that could absorb in the red-orange region.

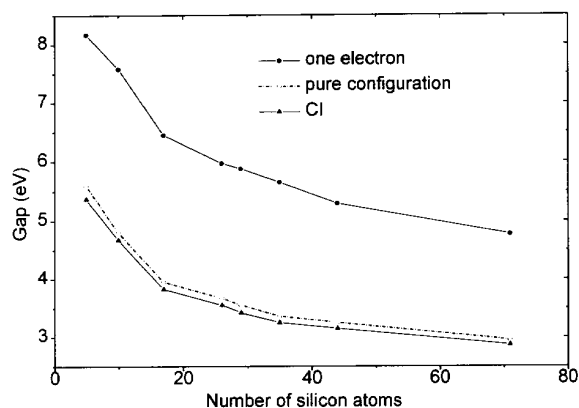


Figure 1. Calculated energy of the lowest allowed optical transition for the H-terminated clusters as a function of the number of Si atoms. (The symmetry and composition of the individual clusters is described in the text.) Triangles: correlation is fully included through Configuration Interaction (CI). Open circles: correlation is partially included by calculating the energy of the most relevant pure excited configuration (for these clusters it is always the HOMO-LUMO excitation). Full circles: single-particle transition between the HOMO and LUMO of the ground electronic state (no correlation included). The lines are just a guide for the eye.

Previous theoretical work on hydrogenated small Si clusters usually neglected correlation altogether, optical properties being extracted from HOMO-LUMO differences^[11–14]. Exceptions are the works of Kumar *et al.*^[15] and Wang and Zunger^[16]. The first authors used however the MNDO-AM1 hamiltonian in the PM3 parametrization^[22]: apart from the fact that PM3 is still a molecular parametrization, the hamiltonian itself is better adapted for the calculation of geometries. They obtain absorption energies of ~ 3.4 eV, and a Stokes-shift of the order of 0.6 eV for the smaller clusters. Wang and Zunger work within the Local Density approximation, which includes and usually overestimates correlation in isotropic form; a point worth noting is that the dielectric function was extrapolated from the bulk crystal to the small particles. Our main results seem however to agree with the predictions of the authors, in that the absorption appears too high to account for the optical properties of porous silicon.

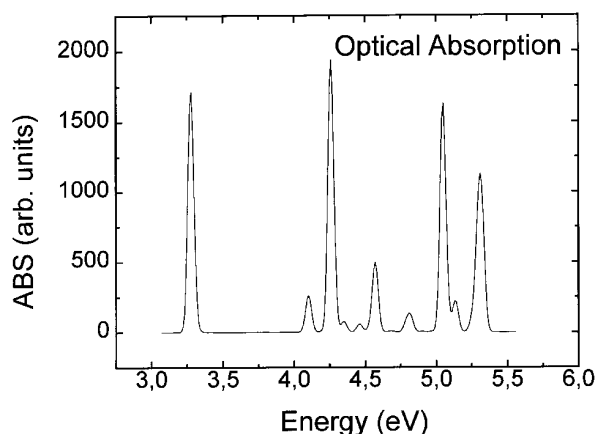


Figure 2. Optical absorption spectrum calculated for the $\text{Si}_{35}\text{H}_{36}$ cluster by including correlation through CI. The lines were gaussian-broadened by 0.01 eV.

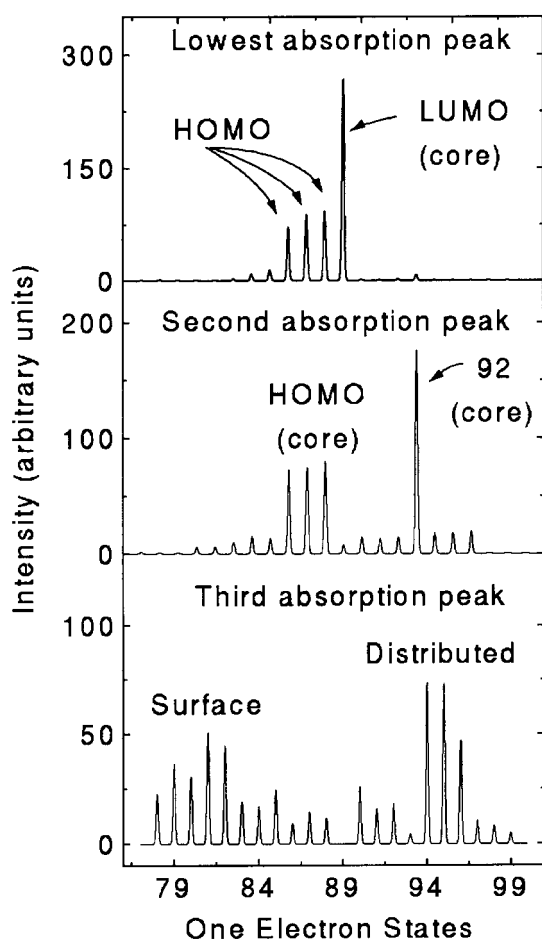


Figure 3. The origin of the absorption peaks of the $\text{Si}_{35}\text{H}_{36}$ cluster (~ 3.25 , 4.25 and 5.05 eV) is analysed by plotting the weight of the single-particle states contributing to the transition (see text). The single-particle levels in the abscissa are numbered by integers indicative of the energy ordering; the Highest Occupied Molecular Orbital (HOMO) is triply degenerate (states 86 to 88), while the Lowest Unoccupied MO (LUMO, state 89) is singly degenerate. The HOMO-LUMO single-particle transition is therefore clearly the dominating contribution to the lowest transition.

We now analyse the origin of the low-energy transitions for a particular cluster (results are very much the same for any of the largest ones). In Fig. 2 we show the optical absorption spectrum obtained for $\text{Si}_{35}\text{H}_{36}$. The three main peaks are resolved into one-electron-transition contributions in Fig. 3, where we project the determinantal states appearing in the CI in terms of single “hole” or “electron” states. Note that the horizontal axis reports eigenvalue numbers, not energies. It is clearly seen that the lowest one-electron transition dominates the first peak: we may thus identify the optical transition as mainly derived from the first (HOMO-LUMO) single particle transition. For the higher-lying states there is already a significant configuration mixing.

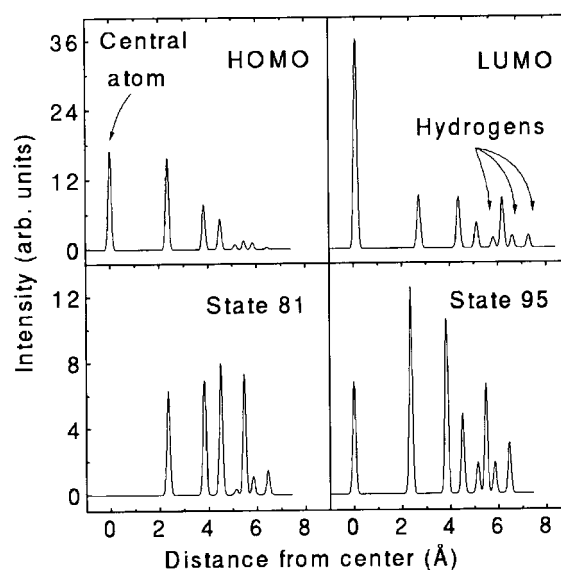


Figure 4. Spatial localization of the HOMO and LUMO for the $\text{Si}_{35}\text{H}_{36}$ cluster: The probability density associated to a typical atom in a given shell is plotted as a function of its distance r from the center of the cluster. All the peaks correspond to Si shells, except those marked by arrows corresponding to the hydrogen shells at the surface of the cluster. Clearly the most important contribution comes from the internal crystalline-like Si shells. We show also two other states near the gap, occupied (state 81) and unoccupied (state 93), that represent more distributed probability densities, and that are important contributions for the second and third absorption transitions; we see that even for these states the surface is not dominant.

To analyse the origin of the first transition, we now resolve the contributions to the HOMO and LUMO from different atoms of the cluster (Fig. 4). This is obtained by simply summing the probability densities associated to the orbitals of all the atoms which belong to a given shell in the cluster (sitting at a given distance from the center); the result is then divided by the number of atoms in the shell for normalization. (For example, in this $\text{Si}_{35}\text{H}_{36}$ cluster there is a central atom, a first shell of 4 Si atoms, then the second and third shells have 12 Si atoms, and the fourth shell has 6 Si atoms; all the hydrogens form 12-atom shells). From the spatial localization of the HOMO (“valence-band top”) it appears that the internal shells of Si atoms account for almost 80 % of the orbital distribution, while the most important individual contribution comes from the central atom (Fig. 4). The same analysis applies to the LUMO spatial distribution. The contribution from the hydrogen atoms is very small, and this happens consistently for all states close to the gap, as we exemplify in Fig. 4. In accordance with previous theoretical results, both on small hydrogenated particles^[15,16] and on hydrogenated Si-surfaces, we find the hydrogen-related one-electron states around 4 eV below the valence band maximum. As a result, we find that all optical absorption below 5 eV has crystalline character.

In summary, we have found that already for this size of particles, with diameters as small as 10 – 20 Å, the vibrational properties show crystalline features. In this sense, the characteristic dimensions inferred by Schuppler et al.^[10] appear to be compatible with the bulk-like phonon frequencies observed in Ref.21. Also, we find that the optical absorption below 5 eV originates from internal shells of Si atoms, and exhibits a crystalline behavior. On the other hand, the emission in the red-orange region is not expected to be directly associated with this absorption, since it would imply a very large Stokes shift.

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