**Structural and Opto-Electronic Properties of silicon Quantum Dot**

**Abstract :**

In this thesis, we investigate the effects of size and hydrogen passivations on the structural, electronic and optical properties of silicon quantum dots. First principles calculations have been carried out to investigate the band gap as a function of the size of Si quantum dots up to 64 atoms per dot with and without surface passivation. In our simulation, the structures of the quantum dots were relaxed and optimized before and after passivation. It is found that the gap increases more for hydrogenated surface than unpassivated one. Thus, both quantum confinement and surface passivation determine the optical and the electronic properties of Si quantum dots. The effect of passivation of the surface dangling bonds by hydrogen atoms and the role of surface states on the gap energy is also examined. The importance of the confinement and the role of surface passivation on the optical effects are also discussed. For the hydrogen passivation effects, the energy gap is larger compared to corresponding pure silicon quantum dots. The optical properties of such dots are experimentally found to be strongly influenced by quantum confinement effects. We found that a hydrogen atom affects the ground state geometry, the total energy and the energy gap of Si quantum dots. Our results show that the addition of hydrogen can cause changes in the electronic structure of a silicon quantum dots, though the geometry is not much affected. Passivations with hydrogen atoms have significant influence on the spatial distribution of the highest-occupied and lowest-unoccupied molecular orbitals. The increase in the magnitude of the binding energy is mainly due to the quantum confinement Effect. The nanocrystal band gap increases with decreasing size down to about 1.5 nm diameter in both passivated and unsaturated nanocrystals, as expected due to a quantum size effects. Thus, both quantum confinement and surface passivation determined the optical and the electronic properties of Si quantum dots. The influence of hydrogen on optical absorption spectra, the static dielectric constant and radiative lifetimes is analyzed in our calculations. In particular, we calculated for Si nanoparticles the dependence of the absorption threshold on size and hydrogenation, the recombination rates, and we demonstrated that in the silicon quantum dots exhibit a reduced quantum confinement effect. We show that theory can help in understanding the microscopic processes important for devices performances.

**General Introduction:**

Semiconductor nanostructures, namely, quantum dots and quantum well wires have attracted a lot of interest due to their new electronic and optical properties that can be modified artificially. Dimensional nanomaterials present fundamentally different physical concepts to conventional bulk materials because of their unique density-of-states as well as optical and electronic confinement. The energy spectrum becomes discrete, measured as quanta, rather than continuous as in bulk materials. Quantum effects become dominant when the nanometre size range is reached, thus accounting for changes in the physical properties of nanostructures, as is the case for the increase in surface area to volume ratio altering mechanical and thermal properties of materials. Here, the geometry of the material can dictate drastic effects on quantized states. As a result, the band gap becomes size dependent and this is known as the quantum confinement effect. This implies that the nanomaterials may exhibit some interesting properties which are not known to the bulk material. Very often, these properties of nanomaterials are tunable via the control of particle size, which allows the engineer to design the growth process according the requirements and desired applications of the final nanodevice.

The challenge is therefore to create functional nanomaterials with a narrow size distribution, and subsequently to elucidate the relationships between properties, size, structure and interfacing with the substrate. The synthesis of nanomaterials with controlled dimensions, shapes, and orientation on the substrate is non-trivial. It is important to consider the suitability and reproducibility of the method for large scale synthesis, as well as the compatibility and ease of integration into conventional microelectronic processing methods. The research of the last decade has been devoted to the attempts of having light-emitting silicon devices. Using both the lithographic-epitaxial and the chemical synthesis techniques, the fabrication of silicon nanocrystals have had an enormous progress in the last years, and sharper and sharper nanocrystal size distributions have been obtained [1-4]. An important goal was the discovery of a strong photoluminescence from porous silicon, which constituted a very easy and economic way for having high-performance photoluminescent silicon structures [5].

The huge efforts made towards matter manipulation at the nanometer scale have been motivated by the fact that desirable properties can be generated just by changing the system dimension and shape. At confined dimensions, optical properties of matter are often altered. For example, elemental silicon (Si) possesses very different properties as a function of size. While silicon in its bulk form is the dominant material for making electronic devices, it has poor optical properties for optoelectronic devices such as solar cells or lasers. However, the poor optical properties of silicon in the bulk form can be dramatically altered at nanoscale dimensions: The band gap in silicon can be blue shifted from the infra-red to the optical region as a function of size. One of the first manifestations of this effect was observed in porous silicon, which exhibits remarkable room temperature luminescence [6,7]. Since the phenomenon of visible photoluminescence (PL) in Si was first discovered by L. T. Canham [8] in the early 1990s, many researchers have conducted experimental and theoretical studies in the direction of Si luminescence. After the discovery of visible photoluminescence in porous silicon (PS) and in Si nanostructures [9-11], the possibility of tuning the optical response of Si nanosized materials by modifying their size has become one of the most challenging aspects of recent semiconductor research due to their natural compatibility with silicon based technologies [12].

In 1992, Proot *et al.* [13] calculated the electronic structure of spherical Si crystallites with diameter up to 4.3 nm using the linear combination of atomic orbital framework. They found that the variation in the optical band gap with respect to the cluster size is in excellent agreement with experimental results [14]. They also estimated an increase of the radiative efficiency of Si PL due to the confinement that leads to a spreading of the wavefunctions in the reciprocal space. At almost the same time, Delley *et al.* [15] using first principles densityfunctional theory (DFT) [16,17] studied visible luminescence in Si nanoclusters ranging up to 3 nm. Their results suggest that the band gap scales linearly with the cluster diameter. They also found that the dipole transitions across the gap in Si nanoclusters are symmetry allowed, in contrast to the dipole-forbidden transitions in a bulk Si lattice. In addition, Wang *et al.* [18] investigated the near-gap electronic structures of Si nanoclusters with size up to 3.7 nm using a plane-wave pseudopotential method. Their results were in a good agreement compared both with experiments and all electron calculations [19].

Although the above theoretical studies [20-22] consistently showed that the gap in a Si nanocluster can be changed by varying its size, semi-empirical modifications have to be implemented to the gap when compared with experimental optical gaps. For example, the value of 0.6 eV has been added to theoretical gaps in the reference [21]. This is because the electron self-energy and the screened electron-hole Coulomb attraction are not correctly taken into account in the calculations, including those obtained using DFT. With the above methods, researchers have calculated accurate optical gaps in Si clusters, and the gaps exhibit strong size dependence. According to quantum confinement effects, the optical gap in Si cluster of 2.0 nm is around 2.6 eV and the gap of the 1.5 nm cluster is approximate 3.5 eV. It has been reported that besides the quantum confinement, the optical gaps of Si clusters are showed to substantially vary through surface passivation. For example, in a spherical Si cluster containing 35 Si atoms, the DFT predicted an energy gap of 3.4 eV for Si35H36 (surface dangling bonds saturated by 36 hydrogen atoms). Their study suggests that hydrogen and other single bonded atoms show similar gaps. Finally, except for quantum confinement and surface passivation, researchers are investigating other factors that may further modify the energy gap [23, 24]. Those factors include doping or defects. Since then, the optical properties of silicon nanocrystals have been studied extensively in both experimentally and theoretically, but still the exact atomic structures and their relations to the optical properties are unclear [21,22]. Especially, the origin of the photoluminescence in nano-silicon is still not understood and is under debate.

Recently, the discovery of optical gain from silicon nanocrystals has suggested the possibility of a silicon-based laser technology. From the theoretical point of view, still today the subject is not completely clear. While the quantum confinement effect has been recognized as the major cause of the photoluminescence, many doubts remain on the way in which the phenomenon takes place. Several mechanisms have been proposed, the most probable of which are the quantum confinement effect, different defects in the surface such as oxygen or hydrogen defects or dangling bonds, and suboxide formation. Quantum confinment effect in the nanocrystallites opens up the energy band gap as well as relaxes the selection rules for radiative transmissions giving rise to photoluminescence in the visible range for crystallites size below ~5nm. A key attribute of porous silicon is the localization of excitations to nanoscale dimensions. This form of silicon could be a good optical material, if technological issues can be resolved. To capitalize properly on such phenomena, a deeper understanding of the optical properties of matter will be required. This thesis is the result of a deep work in the understanding of the electronic and optical properties of silicon nanocrystals.

This thesis is motivated by a desire to discover new properties for silicon nanostructures. Most importantly, these new properties are not exhibited by the bulk counterparts, but manifest only in the nanostructured form of Si, suggesting potential applications of “old” silicon in nanoelectronics when it is transformed into nanomaterial by growth techniques. It demonstrates how known silicon can be modified by nanoscale processes to create new properties. A sound understanding of the structural-property relationship allows scientists to deliver silicon nanomaterial of desired properties with synthesis-by-design. The relevance of its properties to nanoelectronics makes it possible candidates for use in future nanodevices. All these issues will be addressed in this thesis. All the key ingredients that make Si quantum dots appealing for optoelectronic applications are discussed in this thesis: quantum size effects make new phenomena appear in silicon, such as optical absorption. In order to explain the PL mechanism in the Si nanostructures due to quantum confinement in the near surface region, we calculate the band gap that is sensitive to the surface effects and the shape of the silicon quantum dots. We found an enhancement of the calculated gap energy when the surface of the dot was passivated with the hydrogen atoms incorporating in the surface of the dot.

**1.1 Motivation and goal**

In this thesis, the electronic and optical properties of spherical nanocrystals are illustrated. A predictive and quantitative modeling as well as a simulation of these quantum dot structures is essential and can help to narrow down the vast design space to a range that is experimentally affordable. Theoretical analysis of the electronic structures and optical properties of silicon nanocrystals using pseudo-potential-DFT method is presented. Precisely the purpose of this dissertation is thus to focus on:

* How quantum confinement affects silicon nanostructure?
* How silicon and its properties behave at nano-scale?
* How computational methods are applied on nanostructures?
* What potential application does Silicon nanostructures in particular and Nanotechnologies in general have?

The objective of this thesis is to model and simulate theoretically the silicon quantum dot topologies and explore their essential physics. In order to clarify the influence of morphological properties, such as size or shape of hydrogenated and unsaturated Si quantum dot on its electronic and optical properties as a function of size (diameter) and photon energy were attempted using pseudo-potential method. The size effect on the energy gap in unsaturated and silicon passivated by hydrogen nanostructures are described in detail. We will show how the structural and electronic properties, such as density of states, band gaps and optical absorption, in unsaturated and silicon passivated by hydrogen dots vary with size. A comparison with the experimental results and the other calculation tools are also discussed. However, the work presented in this thesis gives support to the quantum confinement effect in explaining the electronic and optical properties of band gap nano-sized silicon below 2 nm, as well as highlighting the importance of calculating optical parameters of silicon quantum dots to understand optical properties in the luminescence process.

**1.2 Thesis outline**

In this thesis we study the electronic and optical properties of hydrogenated and unsaturated Si quantum dots by determining the electronic density of states and optical absorption spectra as a function of photon energy and size distribution. The thesis is organized into five chapters. The first chapter of this thesis outlines the physics of quantum dots and physical properties of silicon quantum dots. The concept of quantum confinement and its effects on the density of state and energy gap of nanostructures is discussed in the same chapter. The second chapter is dedicated to the subject of silicon nanocrystal, its formation, characterization and properties. A short review of nanostructures and nanotechnology applications is also reported in this chapter. Moreover, the different synthesis methods of silicon nanostructures and the accompanying characterizations of silicon nanocrystals are illustrated briefly.

The third chapter is an overview of the theoretical background which concerns the pseudopotential method, used in this work for the study of silicon nanocrystals. Pseudo-potential method based on DFT is used to investigate the structural and electrical properties of nanostructures. This method is discussed shortly in the next chapter to apply it in analyzing nanostructures of silicon crystal. The fourth chapter is dedicated to the discussion of the obtained results. In the first section, this is based on the evaluation of the structure and stability for different hydrogenated and unsaturated Si quantum dots, in order to compare the data from the relevant literature. The second section accounts for the study of the elctronic states and optical properties of the silicon nanocrystals. The results focus mainly on how the optical absorption spectra are related to the band gap and photon energy for the hydrogenated and unsaturated Si quantum dots. In our calculation of the optical absorption spectra of hydrogenated and unsaturated Si quantum dots, we use the joint dielectric function together with dipole matrix elements of the highest occupied molecular orbitals (HOMO) - lowest unoccupied molecular orbitals (LUMO) states. For hydrogenated and unsaturated Si nanostructures, the energy gaps, the optical absorption, the static dielectric constant, the oscillator strength, and the radiative electron-hole recombination times have been calculated with different size of dots. The fifth chapter finalizes the thesis with the summary and conclusion of the present work and describes the evaluation of optical properties of silicon nanocrystals.