



The Role of Hydrogen on Dielectric Properties of Silicon Nanoclusters

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Abstract

A computer simulation using pseudo-potential approach is carried out to investigate the band gap as a function of the size and the shape of small silicon quantum dots (called Si nanoclusters) having 3 to 44 atoms per dot with and without surface passivation by hydrogen. An empirical pseudo-potential Hamiltonian, a plane-wave basis expansion and a basic tetrahedral structure with undistorted local bonding configurations are used. In our simulation, the structures of the quantum dots are relaxed and optimized before and after hydrogen 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. Visible luminescence is probably due to radiative recombination of electrons and holes in the quantum-confined nanostructures. 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. We investigate the entire energy spectrum starting from the very low-lying ground state to the very high-lying excited states. The results for the sizes of the gap, the DOS and the dielectric function of the size are presented. The importance of the confinement and the role of hydrogen passivation on the optical effects are discussed.

Key words: Pseudopotential, Quantum dots, Confinement, Passivation, Luminescence.

1. Introduction

Nanostructuring of semiconductors is a novel means of developing new electronic and optoelectronic devices. In particular, the discovery of room-temperature visible photoluminescence (PL) from Si nanostructures has stimulated much interest in these particular kinds of nanoclusters and in small semiconductor particles (Canham, 1990; Kanemitsu, 1993). The possibility of tuning the optical response of Si nanomaterials by modifying their size has become one of the most challenging aspects of recent semiconductor research. It has been established that quantum confinement (QC) can modify the energy gap such that visible luminescence is produced as experimentally observed (Kanemitsu, 1993; Bettoti, 2003). The porous Si and nanocrystalline Si (Si-nc) with hydrogenated and oxygenated surface has received extensive attention. Optical gain, observed in Si-nc has given further impulse to nanosilicon research. Despite of numerous proposed models to explain the luminescence, including QC, surface states, defects in the oxides and chemical complexes, however, the mechanism of visible PL is far from being understood (Huaxiang, 1993; Ghoshal, 2011; Ghoshal, 2007; Zunger,1996; Liu, 2001; Delley, 1993; Wolkin, 1999; Guerra, 2009). The QC alone cannot interpret the essential features of the PL.

The quantum efficiency of such systems is increased to 1-10% as opposed to 10^{-4} % in bulk Si. It has been surmised that these nanostructures and the porous form of Si have a direct band gap and emit light from violet to red, depending upon the size of the nanostructures (Ghoshal, 2011; Ghoshal, 2007; Zunger,1996; Liu, 2001). Possibly, the luminescence properties may be related to different Si compounds, to surface defect states or to a mechanism different from usual radiative recombination. Many issues such as the size-dependent band gap, the density of states (DOS), the dielectric function and the influence of surface passivation on the optical properties remain controversial.

In this paper, using empirical pseudo-potential method, we investigate the effect of quantum confinement on the energy gap in Si dots of different sizes and geometry and the role of hydrogen passivation on the optical properties of nanoclusters. The dependence of energy gaps on the surface passivation, the role-played by symmetry, relaxation and on the sizes of the Si-dots is examined in detail. Surface passivation of the dot with hydrogen atoms is modeled through an appropriate pseudo-potential (Ghoshal, 2011; Ghoshal, 2007; Zunger,1996). Our present work provides a more detailed account of the energy gap, the DOS and the dielectric function of the dots size and of the role of surface passivation by hydrogen.

2. Simulation Methodology

Empirical pseudo-potential (EP) plane wave theory is used. The EP approximation allows the wave functions to be expanded using a much smaller number of plane-wave basis states. This approximation exploits by removing the core electrons and by replacing them and the strong ionic potential by a weaker pseudo-potential, which acts on a set of pseudo wave functions rather than the true valence wave functions. Our interest here is to find the size dependence of the gap energy and the near band gap solutions, i.e., the separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the presence of hydrogen at the surfaces of the dots. We solve the effective single-particle Schrödinger equation for different sizes of the quantum dot. Following Zunger and Wang (Zunger, 1996), we use a local pseudo-potential for Si and two different forms of the hydrogen empirical pseudo-potential in order to investigate the role of surface passivation on the optical properties. An ideal un-relaxed structure with a Si-H bond distance of 1.487 \AA is used. The dot wave functions are expanded in a large basis of plane waves by using two different values of the cutoff energies 10 Ry and 20 Ry. Each dangling bond at the Si surface

is connected with a surface atom of H. To study luminescence, we calculated the intensity of the transition matrix elements.

We consider Si dots with atoms arranged in a regular tetrahedral network. A stable configuration for all dots of given sizes was considered when the magnitude of the force acting on each atom was about 10^{-3} eV/Å and the total energy of the configuration was a minimum. The reason for choosing small-sized dots is that it is more convenient to analyze their properties in terms of surface passivation while the underlying physics concerning passivation is the same regardless of the size of the system. The role played by passivation in eliminating the dangling bonds and stabilizing the system for both un-relaxed and relaxed dots has been studied. In considering relaxed optimized dots, we are able to make a further distinction between the case when the dots are first passivated and then relaxed and the one in which the dots are first relaxed and then passivated.

3. Results and Discussion

A three-atom dot with a tetrahedral arrangement joined by a single bond with and without hydrogen at the surface gave energy gaps of ~ 2.270 eV and ~ 2.213 eV, respectively. As we passivate the surface of a 3-atom dot with hydrogen (Si_3H_6) and a 5-atom dot with hydrogen (Si_5H_{10}), the occupied number of level changes and the emerged value of the gap show a change. The same thing is observed for the larger dots and is reflected in their corresponding DOS. Following a similar procedure, we examine all other dots with and without hydrogen atoms at the surface. We found an energy gaps of ~ 1.498 eV and ~ 1.483 eV and for a 44-atom dot with and without hydrogen, respectively.

We present the results of our simulation for the variation of the gap energy for different sizes of the dot in Fig. 1 without surface passivation (empty circles) and with hydrogen passivation (empty squares). The results presented are for relaxed and optimized dots only. We find that the gap energy increases as the number of atoms in the dot decreases, which confirms the stronger confinement for the smaller sizes (Bettoti, 2003). As we increase the number of atoms in the dot and change its geometry, the degeneracies are increasingly lifted, which can be seen from the DOS (Fig. 2). We see that for smaller sizes, the confinement is more, and the degeneracies are higher. As we saturate the surface dangling bonds with hydrogen atoms, there is an enhancement of the gap energy to ~ 0.057 eV for a 3-atom cluster and to ~ 0.015 eV for a 44-atom dot. The degeneracies are also lifted because the presence of hydrogen at the surface imparts an interaction potential that acts as a perturbation. For smaller dots, this effect of delocalization near the surface is less; hence, the degeneracies are more pronounced.

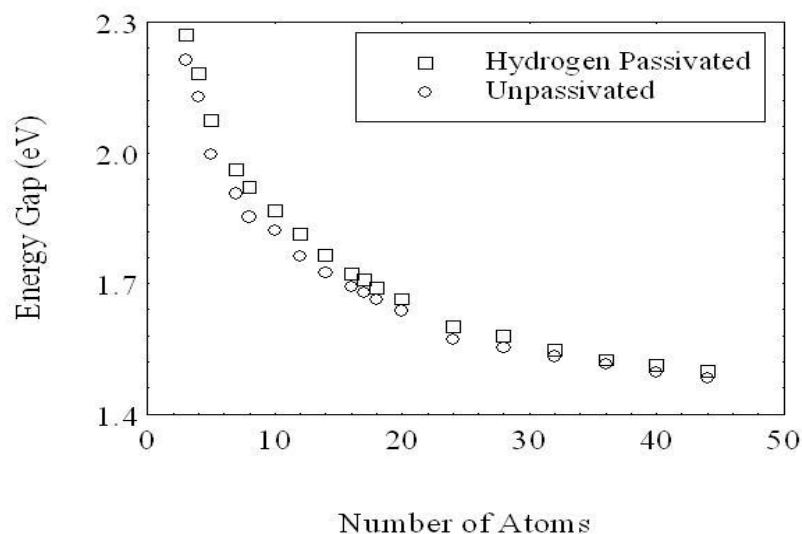


Fig. 1: Variation of the HOMO-LUMO gap energy as a function of the number of atoms in different dots. Empty circles are for the pure clusters (without surface passivation) and empty square boxes for a hydrogen-passivated surface.

The higher gap with passivation is due to the localization of the electron cloud arising from the sp^3 hybridization of the Si-dangling bond with the hydrogen atoms, as reported in the literature (Ghoshal, 2007; Delley, 1993). We observed that for an un-relaxed quantum dot with tetrahedral symmetry, the presence of an undistorted local bonding configuration is sufficient for the appearance of a small vivid energy gap; however, the energy gap does not start at the HOMO. In fact, localized dangling bond states have been found between the HOMO and the lower edge of the energy gap. With hydrogen passivation the localized dangling bond states are eliminated, resulting in a wider and vivid energy gap. Furthermore, the relaxation of these dots does not alter either the structure or the energy gap appreciably. In addition, passivation of these relaxed optimized dots eliminates most of the remnant dangling bonds, but no appreciable effect on the defect states associated with bond distortions has been observed. For the dots with no bond distortion and no overall symmetry, the energy gap as a function of the size of the dots also shows a behavior similar to that of dots having no bond distortion, but tetrahedral symmetry. The dependence of the energy gap on the size showed a behavior similar to that for Si quantum dots with no bond distortion, but possessing overall tetrahedral symmetry. We further observed that the interior of these dots had the bulk-like tetrahedral structure. Our calculation demonstrates that to achieve stability of a dot, a clean gap disappears and dirty gap appears. In other words, a pure and stable Si dot will not have a well-defined gap comparable to the gap of bulk Si.

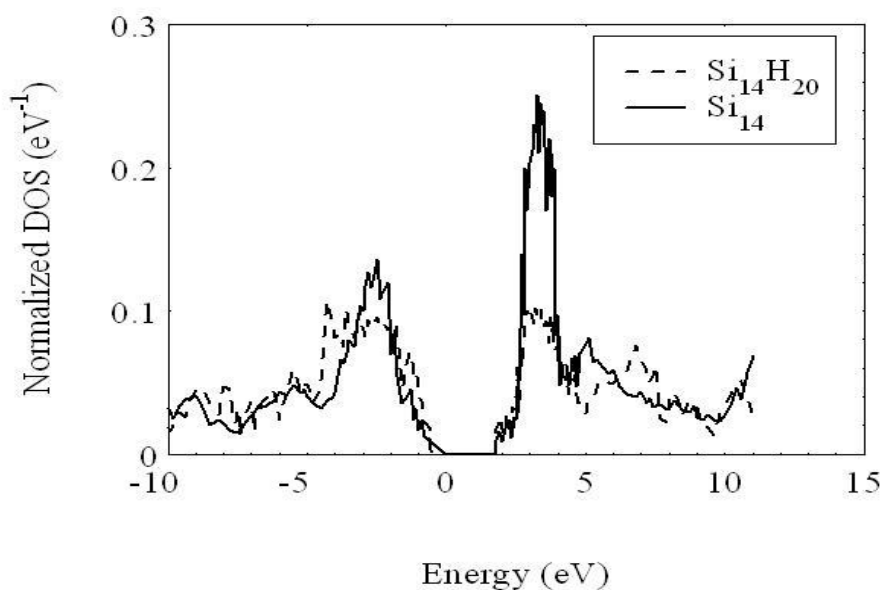


Fig. 2: Normalized DOS for a 14-atom Si dot with and without hydrogen passivation. The upper solid line is for a pure cluster (free surface) and the lower dashed line for hydrogen-passivated surface.

Figure 2 represents the normalized DOS of the spherical quantum dots calculated by using the empirical pseudo-potential moment method. Two different cases for the 16-atom dot are represented, a pure cluster with no surface passivation (Si_{14}) and a hydrogenated surface ($Si_{14}H_{20}$). These systems show molecular features with multiple peaks. We observed that more and more peaks appear due to surface passivation through Si-H bonding. Oscillations are more pronounced for smaller sizes. It is clear from plot that the energy gap increases due to surface passivation. These

results are in conformity with the non-orthogonal tight-binding calculations of Zunger and Wang (Zunger, 1996) and Liu et al. (Liu, 2001). Here, we consider the Si_{16} cluster whose atoms occupy complete shells of a regular tetrahedral network so that the cluster not only possesses local tetrahedral bonding configuration but also an overall symmetry.

The role of hydrogen passivation in eliminating defect states was not analyzed in this study. We do not provide a detailed analysis of the stability and the symmetry of these structures. The DOS plots are displayed with the energy of HOMO for each case set to zero. There is well-defined and substantial clean gap for the DOS corresponding to pure and surface passivated clusters, but this gap does not begin at the energy of the HOMO ($E=0$). There are two prominent peaks at the two extremities of the gap. The first peak is below the HOMO, and the second one is immediately above the gap, i.e., after the LUMO. We also observed that due to the surface passivation with hydrogen, the two broad peaks of the pure cluster are eliminated, and the gap opens up due to the saturation of the dangling bonds by hydrogen passivation. These two broad peaks may be associated with dangling-bond states. The main features of the DOS of the two cases are also very similar. There is, however, some modification in the interior of the band with the appearance of features, which can be identified with Si-H bonding. The existence of a clean and wide gap is perhaps associated with either the local bonding configuration and/or the overall symmetry of the dot.

We turn our attention to the wave function for both the low-lying states and the pair of states near the band gap (HOMO and LUMO states) for all different sizes. We calculate the ground state and excited-state wave functions for all dots by using periodic boundary conditions. The real part of the ground-state wave function has a very strong oscillation near the core region, is highly asymmetric, and decays to a very small constant value beyond a critical distance equal to the size of the box. The imaginary part of the wave function oscillates and then rapidly goes to zero. We found that the surface states contribute differently for the HOMO and the LUMO states. Here, the natures of the oscillations of the wave functions are also different from those of the 3-atom and the 5-atom clusters and clearly reflect the effect of the geometry of the structure, as we mentioned earlier. A similar pattern was observed for all other dots. Our results show that the HOMO-LUMO states are localized and bulk-like instead of surface-like (Huaxiang, 1993; Ghoshal, 2011; Zunger, 1996).

The results for the imaginary part of the dielectric function, $\epsilon_2(\omega)$, for three different kinds of clusters (Si_6H_{12} , $\text{Si}_{10}\text{H}_{16}$, $\text{Si}_{14}\text{H}_{20}$) are presented in Fig. 3. For all these dots, there is a sharp peak near 4.23 eV is observed. For bulk Si the same peak in $\epsilon_2(\omega)$ appears at 4.1 eV, which suggests that the peak for all three quantum dots are bulk like. A side peak is observed on the left side of the main peak for all the clusters that do not present at all in bulk Si, which is the feature of the Si nanostructures. This peak is located at 3.03, 2.14 and 1.81 eV for clusters Si_6H_{12} , $\text{Si}_{10}\text{H}_{16}$ and $\text{Si}_{14}\text{H}_{20}$ respectively. Since $\epsilon_2(\omega)$ is directly related to the absorption coefficient, a peak in the $\epsilon_2(\omega)$ versus $\hbar\omega$ curve indicates that there is a stronger absorption around the energy where $\epsilon_2(\omega)$ has a peak. This feature suggests that, unlike bulk Si there is a comparatively strong absorption of photons at the lower energy region for Si nanostructures. Apart from the occurrence of this peak at lower energy the other interesting feature with surface passivated quantum dots are the shift of this peak towards lower energy and simultaneous decrement in the intensity with increasing cluster size. It confirms experimental observations of the absence of any absorption of photons in case of bulk Si with energy less than 3.0 eV is in agreement with Huaxiang et al. (Huaxiang, 1993).

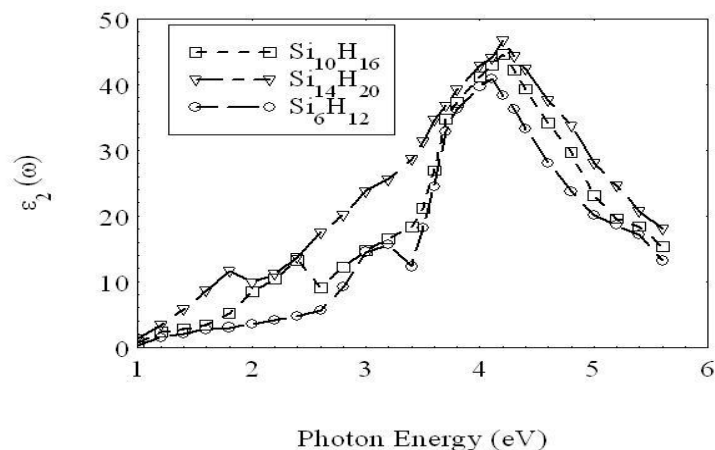


Fig. 3: Imaginary part of the dielectric function versus the photon energy for different dots. Empty circles are for Si_6H_{12} , empty triangles for $\text{Si}_{10}\text{H}_{16}$ and empty square boxes for $\text{Si}_{14}\text{H}_{20}$.

Finally, we compare the energy gap, E_g , and the absorption energy, E_p , corresponding to the peak position of the $\epsilon_2(\omega)$ versus $\hbar\omega$ curve as a function of number of atoms in the cluster as illustrated in Fig. 4. The calculated energy gaps for the three clusters Si_6H_{12} , $\text{Si}_{10}\text{H}_{16}$ and $\text{Si}_{14}\text{H}_{20}$ are turned out to be 2.07, 1.91 and 1.76 eV respectively. It is clear that with increasing cluster size both the energies E_g and E_p decrease and E_g approaches to the value of bulk Si. This particular tendency of the energy variation confirms the quantum size effect. In addition, for all the three clusters considered here the absorption energy is higher than the energy gap. The intensity of photon absorption is intimately related to the DOS near the HOMO-LUMO energy.

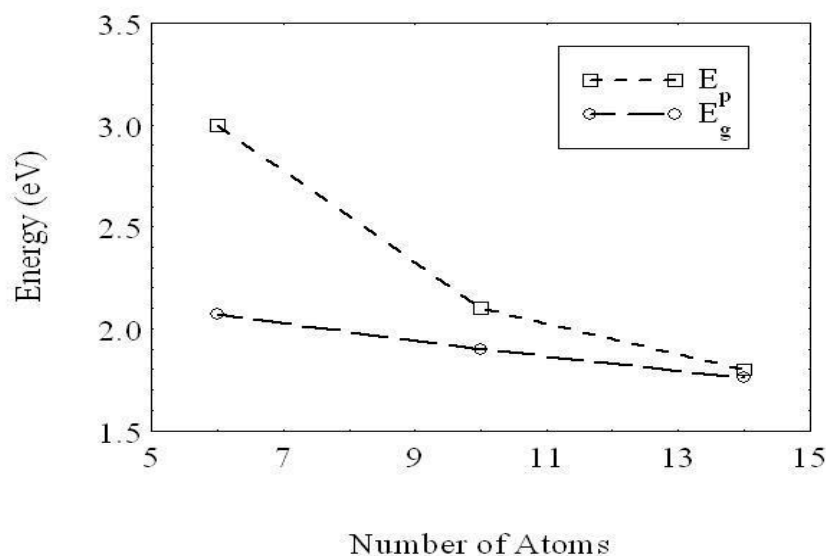


Fig. 4: Energy gap (E_g) and the absorption energy (E_p) calculated from the peak value in $\epsilon_2(\omega)$ versus the number of atoms in different dots. Empty circles are for E_g and empty square boxes for E_p .

4. Conclusions

We have used the empirical pseudo-potential method to calculate the electronic structure of relaxed (optimized) Si quantum dots of different sizes to examine the quantum size effects and the

influence of the surface on the gap energy. Our results show that the gap energy increases as the size of the dot decreases, implying a stronger confinement for smaller dots. This result is in conformity with the earlier observation (Zunger, 1996). The basic characteristics of the quantum dot wave functions indicate that in all cases, the HOMO and the LUMO states are localized in the interior of the quantum dot with zero amplitude on the surfaces. Thus, from the results for the dielectric function, we conclude that finely structured Si appears to be capable of showing a very high luminescence in the visible range as observed experimentally. The calculated DOS for larger dots resembles to bulk whereas smaller dots are like molecular structures. Therefore, we conclude that surface passivation, in addition to the quantum confinement effect, plays an active role in deciding the optical properties and electron correlation of Si nanostructures.

The results for the DOS and dielectric function are in good qualitative agreement with the non-orthogonalized tight binding and first-principles pseudo-potential calculations of others (Huaxiang, 1993; Delley, 1993; Guerra, 2009). Our results provide the theoretical evidence that the emission energy of small spherical Si nanocrystallites can be tuned in the visible range by controlling their sizes useful for high-quantum-yield light-emitting devices as predicted (Guerra, 2009). It is shown that for the hydrogen passivated Si nanostructures; a peak in the lower energy region of the imaginary part of the dielectric function appears in comparison to the bulk Si. Our observations for the dielectric function show that the luminescence and the absorption properties are intimately related to the nanometer size of the dots. To understand the detail mechanism of luminescence, it is worth looking at the luminescence efficiency as a function of crystallite size and surface passivation.

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References

- Bettoti, P., Cazzanelli, M., Dal Negro, L., Danese, B., Gaburro, Z., Oton, C. J., Vijaya Prakash, G., & Pavesi, L. (2003). Silicon nanostructures for photonics. *Journal of Physics: Condensed Matter*, 14, 8253-8281.
- Canham, L. T. (1990). Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers. *Applied Physics Letters*, 57(10), 1046-1048.
- Delley, B. & Steigmeier, E. F. (1993). Quantum confinement in Si nanocrystals. *Physical Review B*, 47, 1397-1400.
- Ghoshal, S. K., Mohan, D., Kassa, T. T., & Sharma, S. (2007). Nanosilicon for photonic applications & references therein. *International Journal for Modern Physics B*, 21, 3783-3793.
- Ghoshal, S. K., Sahar, M. R., & Rohani, M. S. (2011). Investigation of optical effects in silicon quantum dots by using an empirical pseudopotential method. *Journal of Korean Physical Society*, 58(2), 256-264.
- Guerra, R., Marri, I., Magri, R., Samos, L. M., O. Pulci, Degoli, E., & Ossicini, S. (2009). Silicon nanocrystallites in a SiO₂ matrix: role of disorder and size. *Physical Review B*, 79, 155320-155332.

Huaxiang, Fu, Ling, Ye., & Xide, X. (1993). Optical properties of silicon nanostructures. *Physical Review B*, 48, 10978-10981.

Kanemitsu, Y. (1993). Slow decay dynamics of visible luminescence in porous Si: hopping of carriers confined on a shell region in nanometer-sized Si crystallites. *Physical Review B*, 48(16), 12357-12360.

Liu, L., Jayanthi, C. S., & Wu, S. Y. (2001). Factors responsible for the stability and the existence of a clean energy gap of a silicon nanocluster. *Journal of Applied Physics*, 90, 4143-4146.

Wolkin M. V., Jorne, J., Fauchet, P. M., & Delrue, C. (1999). Electronic states and luminescence in porous silicon quantum dots: the role of oxygen. *Physical Review Letters*, 82, 197-200.

Zunger, A. & Wang, L. W. (1996). Theory of silicon nanostructures. *Applied Surface Science*, 102, 350-359.