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A theoretical study of various effects on the wavelength of photoluminescence in Si nanostructures

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Abstract. The photoluminescence in Si nanostructures is studied theoretically through the effects of size, shape and condition of the cluster surface on the energy gap of the Si cluster. Si clusters with a spherical shape or columnar shape are considered. The effect of the condition of the cluster surface is investigated through the chemisorption of hydrogen atoms at the surface. It is found that the energy gap of a cluster decreases with increase in cluster size. For the cluster to simulate an Si column, the calculated energy gap can fall into the energy region of visible-light luminescence with decrease in the cluster size. In the size range (less than 20 Å) considered, the energy gap of the cluster is strongly dependent on the shape, and the surface condition might be important for the determination of the electronic structures of Si nanostructures. These results might be useful in the understanding of photoluminescence in porous Si. The electronic structures of clusters are also investigated in detail.

1. Introduction

Silicon has been the basic material for semiconductor integrated circuits for a long time. Many semiconductor technologies have been developed for this material in past decades. However, owing to its indirect and relatively small band gap, silicon has not been considered to be a good material for optical applications. Several attempts have been made to achieve efficient light emission in Si-based materials such as $\text{Si}_x\text{Ge}_{1-x}$ superlattices [1], $\alpha\text{-SiO}_2\text{:H}$ [2] and $\alpha\text{-Si:H}$ [3]. While some progress has been made, there is still a long way to go before sufficient light efficiency of practical interest is achieved. Another approach from which some novel optical properties of silicon might be obtained in band structure when the fabricated Si structure is small enough has been proposed by Uhlir [4]. Recently, it was reported that a high radiative efficiency can be achieved in porous Si [5,6]. By simple electrochemical dissolution in HF-based solutions, porous Si with efficient visible-light emission at room temperature can be made. This makes porous Si a very promising candidate for optical devices. Since then, much research has focused on the mechanism of photoluminescence in porous Si [7,8] with the purposes of both understanding the basic physics underlying the photoluminescence in porous Si and finding some means by which the photoluminescence in porous Si can be effectively controlled for technological applications. Generally, the size of porous Si falls into the range of several nanometres (about 3 nm) [6,12]. Therefore, it is necessary to carry out some research on the electronic structures of Si nanostructures. Up to now, there have been only a few theoretical reports on the electronic structures of Si nanostructures

[14, 15]. Ren and Dow [14] have given a detailed calculation of the band formation of Si clusters with increase in cluster size in their paper using the tight-binding method. However, the effects of the cluster shape and the surface condition were scarcely discussed therein.

In this paper, a theoretical study of quantum size effects in Si nanostructures will be presented. The energy gaps (called the band gap in the literature on band structures) for Si clusters with different shapes and different sizes are calculated. Clusters with a spherical shape and clusters with a columnar shape are adopted to simulate systems with three-dimensional (3D) and two-dimensional confinements, respectively. In addition, the electronic structures of Si clusters with and without hydrogen adsorbates at the surface have also been studied. These studies might be useful in the understanding of the mechanism of photoluminescence in porous Si, although the sizes of the clusters considered here are not as large as those of porous Si. It is found that, for clusters with either a spherical shape or a columnar shape, the energy gap decreases with increase in the cluster size. When the size is less than 20 Å, clusters of spherical shape have much larger energy gaps than those with the same size of columnar shape. This suggests that there exists a strong dependence of energy gap on the dimensionality of confinement. Calculations also show that, for sizes less than 20 Å, the chemisorption of hydrogen atoms at the cluster surface can significantly change the energy gap. The change in energy gap results from the fact that both the maximum valence level (MVL) and the minimum conduction level (MCL) for clusters with a spherical shape and the MVL for clusters with a columnar shape are obviously affected by the chemisorption of H atoms. This indicates that the condition existing at the surface might have a great influence on the photoluminescence in Si nanostructures when the size is not large enough.

2. Methods

The energy gap is calculated using the charge self-consistent extended Hückel method taking into consideration the charge transfer between surface atoms and inner atoms of the cluster. The method, the details of which have been described elsewhere [10, 11], will be summarized as follows. In the framework of the LCAO method, the wavefunction of the system is expanded as

$$\Psi(r) = \sum_{\mu i} C_{\mu}(i) \Phi_{\mu}(r - R_i)$$

where Ψ is the wavefunction of the system and

$$\Phi_{\mu}(r - R_i)$$

is the μ th atomic wavefunction of the atom situated at R_i . The atomic wavefunctions used are of the Slater type:

$$\Phi(r) = [(2\xi)^{2n+1}/(2n)!]^{1/2} r^{n-1} \exp(-\xi r).$$

The energy levels are determined by solving the secular equations

$$(H - ES)C = 0$$

where H is the Hamiltonian matrix and S is the overlap matrix:

$$H_{\mu\nu}(ij) = \langle \Phi_{\mu}(r - R_i) | H | \Phi_{\nu}(r - R_j) \rangle = 0.5 K_{\mu\nu} (I_{\mu} + I_{\nu}) S_{\mu\nu}(ij)$$

$$S_{\mu\nu}(ij) = \langle \Phi_{\mu}(r - R_i) | \Phi_{\nu}(r - R_j) \rangle$$

$$I_{\mu} = I_{\mu}^0 - \alpha(Q^0 - Q)$$

$$K_{\mu\nu} = 0.5(K_{\mu} + K_{\nu}).$$

In the above expressions, I_{μ}^0 is the ionization energy of the μ th orbital of a free atom, I_{μ} is the modified ionization energy of the μ th orbital due to the charge transfer while Q is the Mulliken charge population of the atom in the process of self-consistent calculation. α is the modification factor of the ionization energy and K_{μ} is the orbital interaction constant. The parameters K_{μ} and α are determined by fitting the energy levels and atomic Mulliken population of the Si_2 dimer and SiH_4 molecule with the results calculated from the first-principles DV- X_{α} method. The values of these parameters have been used in all the previous calculations [10, 11]. The parameters ξ and I_{μ}^0 are taken from [13] and [16], respectively. The parameters I_{μ} , K_{μ} and ξ for Si and H atoms are listed in table 1. After the convergence of the self-consistent calculation, the MVL, the MCL and the energy levels due to the dangling bonds can be found through analysis of the wavefunctions. Concretely, for the LCAO wavefunction at a certain level, if the coefficients of the corresponding atomic orbitals of dangling bonds of the clusters are relatively much larger, this level can be thought of as characteristic of the dangling bonds.

Table 1. Parameters used in the calculation. The parameters are the orbital exponent ξ , ionization energy I_{μ}^0 and the orbital interaction constant K .

Atom	Orbital	ξ	I_{μ}^0 (au)	K
Si	3s	1.6344	0.4947	1.60
	3p	1.4284	0.2996	1.60
H	1s	1.2000	0.3200	1.20

Clusters of spherical shape are chosen with one Si atom at the centre, while clusters of columnar shape consist of four atomic layers in the Si(111) orientation. In order to simulate the silicon column, pseudo-Si atoms are used to saturate the dangling bonds in the vertical direction of the Si(111) surface on both sides of the four-layer Si atoms. The mean values of the sp^3 hybridization orbitals of the Si atom are adopted for the parameters of the pseudo-Si atoms. Both the spherical and the columnar clusters are shown schematically in figure 1. The calculation results are illustrated in table 2 for clusters with a spherical shape and in table 3 for clusters with a columnar shape.

Table 3. Calculated energy gaps for clusters of columnar shape. In this table, Si' represents the pseudo-Si atom used to saturate the dangling bonds in the vertical direction of the Si(111) surface.

Surface condition	Cluster	Size (Å)	Energy gap (eV)
Without H atoms	Si ₂₆ Si' ₁₂	8.87	3.81
	Si ₅₀ Si' ₂₄	13.30	3.36
With H atoms	Si ₂₆ Si' ₁₂ H ₁₈	11.66	3.07
	Si ₅₀ Si' ₂₄ H ₃₀	16.09	2.55

includes the concrete atomic structure and might be more realistic. It is not difficult to imagine that, when the cluster becomes large, the properties of the cluster will become increasingly similar to those of the bulk. Therefore, the energy gap will be close to the band gap of bulk Si except that some energy levels appear in the gap because of the presence of dangling bonds at the surface of the cluster. The energy gaps of the clusters Si₁₇H₃₆ and Si₃₅H₃₆ in this calculation are slightly different from those of Ren and Dow [14] and ours are about 1 eV larger. This might be mainly due to the consideration of charge transfer between different atoms in this calculation, which is important in determining the electronic structures of a cluster with a very small size.

When hydrogen atoms are adsorbed at the surface of the cluster, the energy gap is significantly reduced in the size dimension considered in the present calculation (less than 20 Å). This indicates that, when the cluster is not large enough, the surface condition of the cluster might have a great influence on the energy gap. In order to understand the influence of the surface on the energy gap more clearly, the energy gaps for clusters Si₃₅H_{*n*} with different numbers 36-*n* of dangling bond are calculated. The results are listed in table 4. With the dangling bonds of the fourth-shell Si atoms in cluster Si₃₅ remaining unsaturated and the others saturated by H atoms, Si₃₅H₂₄ has an energy gap of 5.53 eV, which has decreased greatly in comparison with the energy gap of Si₃₅ (9.07 eV). If some more dangling bonds except those having a (111) orientation in Si₃₅H₂₄ are saturated, Si₃₅H₃₃ has an energy gap of 4.53 eV with three energy levels in the gap produced by the three remaining dangling bonds. From table 4, it can clearly be seen that the different degrees of surface saturation of the Si cluster can change the energy gap on a large scale for clusters of a small size. However, when the cluster becomes sufficiently large, the influence of the surface on the energy gap might not be so significant.

Table 4. Calculated energy gaps for the clusters Si₃₅H_{*n*} of spherical shape with the number of dangling bonds equal to 36 - *n*.

Number of dangling bonds	Cluster	Energy gap (eV)
36	Si ₃₅	9.07
12	Si ₃₅ H ₂₄	5.53
3	Si ₃₅ H ₃₃	4.53
0	Si ₃₅ H ₃₆	4.52

3.2. Clusters with a columnar shape

In the experiments, porous Si samples are usually considered to have an irregular columnar shape like coral after treatment in HF-based solutions. As mentioned above, to simulate porous Si with a coral shape in the calculation, pseudo-Si atoms (labelled Si' in the following) are used to saturate the dangling bonds along the column axis. In order to test the validity of this method, the electronic structures of the cluster $\text{Si}_{50}\text{Si}'_{54}$ in a columnar shape with all the dangling bonds of cluster Si_{50} saturated by pseudo-Si atoms are studied. The similarity between the electronic structure of this cluster and that of the silicon bulk indicates that the saturation of the surface by pseudo-Si atoms is plausible.

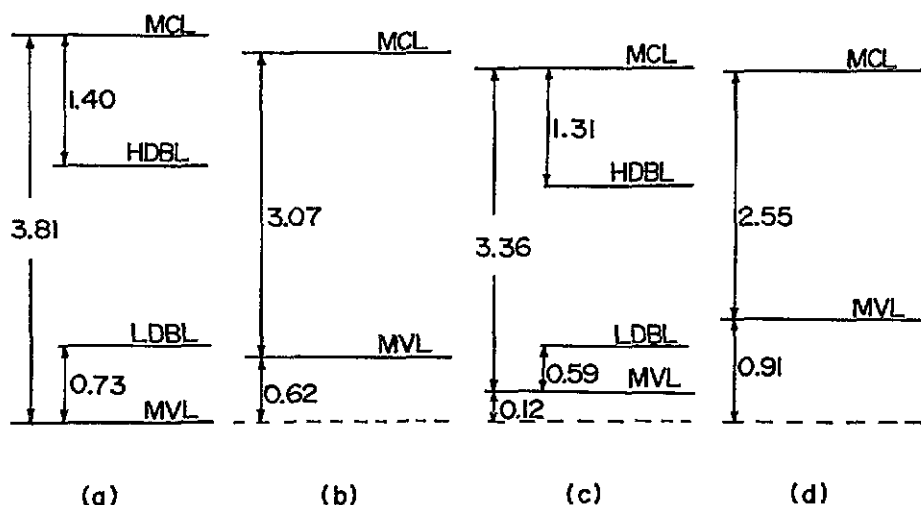


Figure 2. Diagrams of the energy levels calculated for the clusters with a columnar shape. The calculated clusters are (a) $\text{Si}_{26}\text{Si}'_{12}$, (b) $\text{Si}_{26}\text{Si}'_{12}\text{H}_{18}$, (c) $\text{Si}_{30}\text{Si}'_{24}$ and (d) $\text{Si}_{50}\text{Si}'_{24}\text{H}_{30}$. In this figure, MCL, MVL, HDBL and LDBL represent the minimum conduction level, the maximum valence level, the highest dangling-bond level and the lowest dangling-bond level, respectively. The dangling-bond levels between the HDBL and the LDBL are not shown in the figure. The broken line indicates that the MVL of the cluster $\text{Si}_{26}\text{Si}'_{12}$ in (a) is taken as the reference level. The differences between the energy levels are labelled in the figure in electronvolts.

In table 3, clusters of two different sizes ($\text{Si}_{26}\text{Si}'_{12}$ and $\text{Si}_{50}\text{Si}'_{24}$) are considered. The diagram of the energy levels for these clusters is shown schematically in figure 2. First, the size effect on the energy gap is studied when clusters with different sizes have the same surface condition (with H atoms or without H atoms at the surface). For clusters without H adsorbates, when the size of cluster increases from 8.87 to 13.30 Å, the energy gap decreases from 3.81 to 3.36 eV. From this result, it can be seen that the size of cluster has an obvious influence on the energy gap. The

tendency of the variation in energy gap with cluster size is the same as for clusters with a spherical shape. With hydrogen atoms adsorbed at the surface, the energy gaps of corresponding clusters are reduced by about 0.8 eV in the cases considered. The size effect on the energy gap is still obvious. The energy gap decreases from 3.07 to 2.55 eV when the size increases from 11.66 to 16.09 Å. Since porous Si is prepared in HF-based solutions, some hydrogen atoms might be adsorbed at the surface of porous Si. It is natural to consider cluster models with adsorbed H atoms in more detail. For the clusters $\text{Si}_{26}\text{Si}'_{12}\text{H}_{18}$ and $\text{Si}_{50}\text{Si}'_{24}\text{H}_{30}$, the lateral sizes are 11.66 Å and 16.09 Å, respectively; the corresponding energy gaps for these two clusters are 3.07 eV and 2.55 eV. These energy gaps fall into the energy region of visible-light luminescence (1.6–3.2 eV).

To illustrate the concrete electronic structures of clusters with a columnar shape, the cluster $\text{Si}_{50}\text{Si}'_{24}\text{H}_n$ is taken as an example. As shown in figure 2, for the cluster $\text{Si}_{50}\text{Si}'_{24}$ without H adsorbates, the difference between the MVL and the MCL is 3.36 eV. In the energy gap, there exist 30 energy levels owing to the lateral dangling bonds, whose energies spread over a range of about 1.5 eV. The lowest dangling-bond level is 0.5 eV above the MVL while the highest dangling-bond level is 1.35 eV below the MCL. After hydrogen atoms are adsorbed onto the surface, all energy levels in the gap which are due to dangling bonds are removed. The chemisorption of H atoms makes the MVL shift upwards by 0.78 eV and the MCL downwards by 0.05 eV in comparison with the corresponding cluster with a clean surface. It can be concluded that, for clusters with a columnar shape, the chemisorption of H atoms causes an obvious change in the MVL, but little change in the MCL. However, this is not the case for clusters with a spherical shape, where the chemisorption of H atoms causes a large change in both the MVL and the MCL.

From the analysis of the wavefunctions, it is found that, for clusters with a columnar shape with H atoms adsorbed, the LCAO expansion coefficients of H atoms are large at the MVL. This indicates that hydrogen atoms make a great contribution to the MVL. Our analysis of the characteristics of the MVL of clusters with H atoms adsorbed is quite consistent with the experimental result of the large Si–H signal in the transmission of porous Si given by Tischler *et al* [8]. Both the significant change in the energy gap caused by the chemisorption of H atoms and the analysis of the characteristics of the MVL suggest that the surface condition might play an important role in the process of photoluminescence in Si nanostructures, at least in the size range considered in our calculation.

It is interesting to make a comparison between the results in table 2 and those in table 3. The cluster $\text{Si}_{29}\text{H}_{36}$ in table 2 and the cluster $\text{Si}_{26}\text{Si}'_{12}\text{H}_{18}$ in table 3 have almost the same size, but their energy gaps are quite different from each other. For clusters without hydrogen adsorbates, the difference between the energy gaps of the spherical cluster Si_{29} and of the columnar cluster $\text{Si}_{26}\text{Si}'_{12}$ is much more significant. Hence, the energy gap of the cluster is strongly dependent on the dimensionality of confinement.

4. Conclusion

In summary, the effects of size, shape and condition at the surface on the energy gap of Si clusters are investigated. The energy gaps of the clusters with the same shape decrease with increase in the cluster size. In the size range considered, the energy

gaps of the clusters are greatly affected by the shape of the clusters. The condition at the surface of the cluster might also play an important role in the determination of the energy gaps. These results might be useful in the further understanding of the mechanism of photoluminescence in porous Si.

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