Study of Band gap of doped silicon nanocrystal
S Joshi, S Kausar, G Singh

Abstract
Silicon nanowires (SiNWs) are attracting great interest as the most promising building blocks for future nanoscale electronic devices. Remarkable development has been achieved toward the goal of application of SiNWs in industry in the past decade. The small sizes of SiNWs make their electronic properties strongly dependent on growth direction, size, morphology and surface reconstruction. A well-known example is the size dependence of the electronic band gap width of SiNWs irrespective of wire direction. As the wire diameter decreases, the band gap of the nanowire widens and deviates from that of bulk silicon gradually. Moreover the orientations of the wire axis and the surface have a great effect on the electronic properties of SiNWs. In this work, systematic studies on the electronic structure of SNWs were conducted based on Effective mass approximation. In this paper the diameter of nanocluster through which nanowire are made is calculated and the size of nanocrystal depends on number of atoms present in the nanocrystal and after calculating the size of nanocrystel the band gap of silicon nanowires doped with little amount of aluminum is calculated. And after the calculation interesting finding are obtained it is found that the band gap decreases with increasing size of nanocrystal and the band gap that calculated is different from the bulk silicon. And it is also found that the band gap of doped silicon nanowire is different from bulk material. In this paper, systematic studies on the electronic properties of SiNWs were conducted based on tight binding scheme and parameters, we calculate the band gap energy of doped silicon nanowires by calculating the size of the nanocrystel of the nanowires. Also in this paper it is found that there is effect of temperature on the band gap of doped silicon nanowires. The results which are obtained in this calculation are in excellent agreement with the experimental results.

INTRODUCTION
The scientific field of silicon nanostructures is a fascinating area of material science. The research of the last decade has been devoted to the attempts of having light-emitting silicon devices. Silicon nanowires (SiNWs) are attracting great interest as the most promising building blocks for future nanoscale electronic devices. Remarkable development has been achieved toward the goal of application of SiNWs in industry in the past decade. The optical properties of semiconductor nanocrystals have attracted considerable attention due to their possible applications in quantum dot laser and other devices. The small sizes of SiNWs make their electronic properties strongly dependent on growth direction, size, morphology and surface reconstruction. A well-known example is the size dependence of the electronic band gap width of SiNWs irrespective of wire direction. As the wire diameter decreases, the band gap of the nanowire widens and deviates from that of bulk silicon gradually. 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 nanocrystal size distributions have been obtained. 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 photo luminescent silicon structures. Recently, the discoveries of optical gain from silicon nanocrystals have suggested the possibility of a silicon-based laser technology. From the theoretical point of view, still today the subject is not completely clear. The Tight Binding method, used in this work for the study of the nanocrystals. The advantage in the use of such a method lies in its huge efficiency: Tight Binding is the only method able to study both small and very large nanocrystals. In fact, its short range interaction parameters lead to nanocrystal Hamiltonian matrices really very sparse. This feature has been used through a diagonalization routine having a computational time which scales linearly with the matrix size. The method that we have chosen seems to work very well for the Bulk Silicon and doped silicon. An interesting feature is the existence of an energy gap between the energy of the first transition and the threshold of the absorption cross section. This is an indication that the electronic features of the bulk silicon are
always reacted into the silicon nanocrystal physics. A very nice confirmation of this trend is the k-space projection of the nanocrystal states, which gives a fair explanation of this phenomenon.

Since the fundamental paper of Slater and Koster (SK) [1], the Tight Binding interpolation scheme (TB) has been a powerful tool for electronic spectra and density of states calculations of crystalline structures. The method is based on the expansion of the wave functions into linear combinations of atomic orbitals (LCAO), with Hamiltonian matrix elements parameterized in such a way to reproduce first-principles calculations and/or experimental data. Compared to the methods based on the Plane Wave basis sets (PW), the TB scheme is very efficient in problems where localized functions are required. In fact, the method has been widely used especially in impurity states calculations [2], where it is computationally advantageous because it only needs a small number of localized orbitals. With the increasing of computer performances, ab initio TB models have been attracting a great interest. In fact, the TB interpolation schemes are empirical tools, often called Empirical Tight Binding, in which we usually do not have an explicit knowledge of neither the basis functions, nor the real space Hamiltonian. On the other hand, the ab initio approaches are based on the explicit construction of both the localized atomic orbitals and the Hamiltonian matrix elements. The ab-initio TB models can be very accurate and powerful, but they are computationally more demanding. Therefore, for the great simplicity of the original SK formulation, and the huge precision reached in getting accurate band structures, the Empirical TB models are still today very attractive calculation tools.

ETB scheme as it is usually used in band structure calculations. Empirical Pseudo potential method (PP), often used as an important comparison scheme, it is known for its great efficiency for the bulk structures, and the huge computational effort that it requires for the nanocrystals. we have compare several TB parameterizations available in literature for the crystalline silicon. The first explanation for the size dependence of electronic properties in nanocrystals was given by Efros[3]. It is depend on the effective masses of electron and hole and it is known as effective mass approximation(EMA), it is solved by taking the various choices for the electron and hole wave functions and solving the effective mass equation variationally. In most EMA calculations, the confining potentials for the electron and the hole have been assumed infinite. Therefore, the electron and the hole wave functions vanish at and beyond the surface of the nanocrystal, without the possibility of any tunneling. In the strong confinement regime, where R, the nanocrystal radius, much smaller than the Bohr exciton radius, Brus [4] proposed the following expression for the band gap of the finite sized system:

\[
E(R) = E_g + \frac{\hbar^2}{2\left(1/m_e^* + 1/m_h^*\right)}\pi^2/R^2 - 1.786e^2/\epsilon R - 0.248E^*_{Ry}
\]

Where \(E_g\) is the bulk band gap. The second term is the kinetic energy term containing the effective masses of the electron and the hole, the third term arises due to the Coulomb attraction between the electron and the hole and the fourth term due to the spatial correlation between the electron and the hole which is generally small compared to the other two terms. in this relation the interaction between doped and bulk atom is considered and also temperature dependence of band gap is calculated by using following formula [12]

\[
E(R) = E(R) - \beta T
\]

**TIGHT BINDING MODEL**

The starting point of every Tight Binding model is the definition of a suitable set of atomic-like orbital. In the following we will consider bulk crystalline structures doped with Aluminium, with atoms located in the positions of a Bravais lattice. The TB orbitals are localized at the atomic positions, and they are usually chosen in such a way to transform into each other under the crystal point group operations, according to a suitable irreducible representation (see Appendix(A)for more details on symmetries).

In a first step, we have calculated the energy levels for a set of hydrogenated spherical nanocrystals, with increasing size. For each nanocrystal, the effective diameter is calculated as follows [5,6].

\[
D = a \left[\frac{3N}{4\pi}\right]^{1/3}
\]

Where \(a\) is the lattice constant and \(N\) is the number of atom present in the nanocrystal.
Table 1 lists the number of atom present up to a given shell and the diameter of the nanocrystal for doped silicon structure. The starting point of every Tight Binding model is the definition of a suitable set of atomic-like orbitals. In the following we shall only consider bulk crystalline structures, with atoms located in the positions of a Bravais lattice with a basis; we indicate with \( \mathbf{R} \) the lattice vectors, and the atomic positions within the unit cell. Therefore, all the atoms contained in the structure lie in the positions:

\[
\mathbf{R}_\mu \equiv \mathbf{R} + \mu. 
\]

In the case of the bulk silicon (diamond structure), the Bravais lattice is an FCC and there are two atoms in the unit cell, whose positions are:

The band structure is now obtained solving the Eigen value problem for the reciprocal space Hamiltonian matrix, for each \( \mathbf{k} \)-vector lying inside the first Brillouin Zone (BZ):

\[
\sum_{\sigma' \mu'} \left[ H_{\sigma \sigma'}^{\mu \mu'}(\mathbf{k}) - E_n(\mathbf{k}) \delta_{\sigma \sigma'} \delta_{\mu \mu'} \right] B_{\sigma' n}^{\mu \mu'}(\mathbf{k}) = 0, 
\]

And the crystalline Eigen states come from the expansion

\[
|n\mathbf{k}\rangle = \sum_{\sigma \mu} B_{\sigma n}^{\mu \mu}(\mathbf{k}) |\sigma \mu \mathbf{k}\rangle. 
\]

The above procedure only requires the knowledge of the interaction parameters in order to calculate the single-electron energy levels of bulk structures. Using symmetries, all these parameters can be reduced to a minimum number. Two factors enter into the definition of a TB scheme: the number of species of atomic orbitals and the number of nearest neighbors that interact with a single orbital. These two factors determine the number of independent parameters. After that a suitable set of independent interaction parameters has been chosen, the next step of the Empirical TB scheme is based on calculating them in such a way to fit, after the diagonalization of experimental data and/or ab initio calculation results of energy gaps and/or effective masses, in high symmetry \( \mathbf{k} \)-points.
have incredibly improved, allowing more complex fitting procedures than in the past. In this way, fitting of a band structure with many independent parameters is now possible, with the result of making TB band structures very close to ab initio results. Even if the first neighbor sp$^3$-TB is nowadays very used [10,11], because of its simplicity in considering only nearest neighbor interactions, better results are obtained using the minimal basis set sp and increasing the number of neighbors interacting with a single orbital.

ENERGY LEVELS

In a first step, we have calculated the energy levels for a set of doped silicon nanocrystals, with increasing size. For each nanocrystal, the effective diameter is calculated as follows [5, 6]. In the bulk, ideal structure, the volume associated to each Si atom is $v_{Si} = a^3/8$ (a ≃ 5.4nm is the lattice constant for silicon lattice doped with Aluminum). The diameter is easily calculated using the relation [9]:

$$D=a\left[\frac{3N}{4\pi}\right]^{1/3}$$

In figure 2.1 a graph between the calculated diameters with number of atoms present in the crystal is plotted. From this graph it is clear that the diameter of nanocrystal increases with the number of atom present in the crystal for a fixed lattice constant.

It is also possible since the bulk silicon is doped with little amount of aluminum and because of this doping the lattice constant of the material can be varied with the position and this time the diameter of the crystal will depend on the lattice constant of the material and this time a graph is plotted between lattice constant and the diameter of the crystal and from fig. 2.2 it is clear that the diameter of the crystal increases with the increasing value of the lattice constant.

In Fig. 3 we show a comparison between our results and other theoretical results for doped silicon nanocrystal through which nanowire is made. Also in this case there is a large scatter of the calculated data, and this is especially true for the ab initio methods. Some considerations can be inferred by the graph. First of all, there is a good agreement with the other important semi empirical method, based on the tight binding method. In figure calculations based on tight binding method is represented by squares and calculation obtained by EMA is represented by triangles. It is worth noting that the calculation based on tight binding method is very similar to our results, with a better agreement for larger nanocrystals. The situation for small nanocrystals is more complicated. Even for data reproduced within the same approach, like the Time Dependent Density Functional Theory (TDDFT), we can have quite different results. The calculation based on Effective mass approximation method is shown by green line.
made by triangle from this graph it is clear that there is a huge difference in the band gap value for the small size nanocrystal that ranges from 12.5nm to 16 nm diameters and this difference in the band gap of the crystal is about 2eV.

**Figure 10**

Figure 3

Figure 11

Figure 4

In fig.4 a graph is plotted between diameter and band gap energy in this graph we have compared the band gap Obtained by tight binding method and effective mass approximation method and also in this Graph the effect of temperature on band gap of doped silicon nanocrystal is considered. In this graph the calculation obtained by tight binding method is represented by squares and calculation based on effective mass approximation method is represented by triangles and the calculation based on effective mass approximation in which the effect of temperature is considered is represented by solid line. This calculation is carried out at room temperature. It is worth noting that the calculation based on tight binding method is very similar to our results, with a better agreement for larger nanocrystals. The situation for small nanocrystals is more complicated. From this graph it is clear that there is a huge difference in the band gap value for the small size nanocrystal that ranges from 12.5nm to 16 nm diameter and this difference in the band gap of the crystal is about 2eV. And from fig.4 it is clear that there is negligible effect of temperature on the band gap of silicon nanocrystal doped with aluminium at room temperature.

**Figure 12**

Figure 5

In fig 5 the comparison between the band gap calculated by EMA method in which effect of temperature is also considered is shown for different temperature and from this graph it is clear that there is a little effect of temperature on the energy band gap of nanocrystal. But if the temperature is increased upto 1000K then the band gap will reduced as shown in fig. in this fig the diamond represent the calculation carried out at 1000k.

**CONCLUSION**

We have calculated the band gap of silicon crystal doped with little amount of alumunium as a function of the nanocrystallite size using the tight binding method in this we have consider aluminium-silicon and silicon-silicon interaction. And also we have calculated the band gap of doped silicon nanocrystal by using effective mass approximation method in this method we have considered the coulombion forces between alumunium and silicon atom and silicon-silicon atom and after it the result obtained by both the method are compared and it is found that It is worth noting that the calculation based on tight binding method is very similar to our results, with a better agreement for larger nanocrystals. The situation for small nanocrystals is more complicated. it is found that there is a huge difference in the band gap value for the small size nanocrystal that ranges from 12.5nm to 16 nm diameter and this difference in
the band gap of the crystal is about 2eV and it is also found that there is negligible effect of temperature on the band gap of silicon nanocrystal doped with aluminium at room temperature but if the temperature is increased up to 1000K then the band gap will reduced. The calculated variations in the band gap over a wide range of sizes are compared with the experimental data and this comparison shows a very good agreement.

References
11. R. S. Sedha
Author Information

Shirish Joshi
Dept. of Physics, Govt. MVM College, Bhopal

Sana Kausar
Dept. of physics, All Saints’ College of Engineering

Gurpreet Singh
Dept. of electronics, All Saints’ College of Engineering Bhopal, India