

Ab-Initio large unit cell calculations of the electronic structure of Si and Ge nanocrystals

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Abstract

Ab – initio restricted Hartree - Fock method within the framework of large unit cell (LUC) formalism is used to investigate the electronic structure of Si and Ge nanocrystals. The surface and core properties are investigated. A large unit cell of 8 atoms is used in the present analysis. Cohesive energy, energy gap, conduction and valence band widths are obtained from the electronic structure calculations. The results are compared with available experimental data and theoretical results of other investigators. The calculated lattice constant is found to be slightly larger than the corresponding experimental value because we use only 8 atoms and we compared the results with that of the bulk crystals, nanoclusters are expected to have stronger directional bonds that in their bulk structure. The surface states are found to be mostly non-degenerated because of the effect of surface discontinuity and the existence of oxygen atoms. Valence and conduction bands are found to be wider on the surface due to the splitting of energy levels due to the existence of oxygen atoms. The present method can be used to investigate the electronic structure of bulk, surface and nanocrystals.

Key words

Nanocrystals,
Surface,
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حساب المبادئ الأساسية ضمن وحدة الخلية الكبيرة للتركيب الإلكتروني لبورتي السليكون والجرمانيوم النانوية

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الخلاصة

تم استعمال نظرية المبادئ الأساسية وطريقة هارتر-فوك المقيدة ضمن إطار خلية الوحدة الكبيرة لدراسة التركيب الإلكتروني لبورتي السليكون والجرمانيوم النانوية. وقد تمت دراسة خصائص السطح والقلب لكلتا البلوريتين باستعمال خلية وحدة كبيرة بثمان ذرات. تم الحصول على طاقة الترابط و فجوة الطاقة و عرض حزمتي التكافؤ والتوصيل من حسابات التركيب الإلكتروني، و من ثم قورنت النتائج التي تم الحصول عليها مع نتائج عملية و نظريه لدراسات سابقة. وقد وجد أن قيمة ثابت الشبكة المحسوبة هي أكبر بقليل من القيمة العملية. كما وجد أن التراكيب النانوية تمتلك أواصر موجهة أقوى مما هي عليه من تلك الموجودة في الحالة الصلبة. كذلك وجد أن حالات السطح تكون غير متحللة بسبب عدم استمرارية السطح ووجود ذرات الأوكسجين. أما بالنسبة لعرض حزمتي التكافؤ و التوصيل فلقد وجد إنها أعرض مما هي عليه للبلورات في حالتها الصلبة نتيجة انشطار المستويات الطاقية لوجود ذرات الأوكسجين. إن الطريقة الحالية يمكن استعمالها لدراسة التركيب الإلكتروني للمادة الصلبة والسطوح والبلورات النانوية.

Introduction

In recent years, Si and Ge have become materials of choice for different applications in the microelectronics industry. The widespread application of Si and Ge is imminent and expected in the near future. Because of its low field mobility, Ge is used for high speed devices, and by mixing Ge and Si, (SiGe), the electrical properties of Si substrates can be tuned to obtain very efficient device performance. As a result of the growing application of Si and Ge nanocrystals in device production, there is an emerging need to study the electronic structure of these crystals [1].

The large unit cell (LUC), which is a kind of supercell methods, was suggested and first applied for the investigation of electronic band structure of bulk materials and in particularly elemental semiconductors in the 70s of the last century. After its success in describing the electronic structure of bulk semiconductors, the method was also applied to a variety of systems. The method was usually coupled with semiempirical methods to overcome ab initio computational difficulties of large scale and deformed systems [2].

In the present work, the electronic and structural properties of the (001)-(1×1) oxygenated surface of Si and Ge have been investigated using ab-initio restricted Hartree-Fock (RHF) theory supercell calculations, also ionization potential and electron affinities are presented for both (8 atoms LUC) core and surfaces [3].

The electronic structure of (001)-(1 × 1) oxidised surface and inner core of germanium nanocrystals (1.5–2.3 nm in diameter) is studied separately by N.H. Aysa[4] using the self-consistent Hartree–Fock method coupled with the large unit cell (LUC) method. The separate evaluation of surface and core electronic structure leads to the exact discrimination between nanocrystal surface and core properties.

Computational Details

We shall perform the core part using the LUC method and the oxygenated (001)-(1×1) surface case that can be added to obtain a complete electronic structure view. The periodic boundary condition (PBC) method available in Gaussien03 program [3] is used to perform the present tasks. The restricted Hartree-Fock (RHF) method (in which all of the electrons are paired, during the solution of the self-consistent field equations, the solution is restricted so that the spatial wave functions for paired electrons are the same) is used for molecules in which all the electrons are paired.

Ab-initio restricted closed-shell and restricted open-shell Hartree-Fock calculations, each corresponding to an average energy of configuration, were carried out on numerous low-lying states of each cluster. (The average energy of configuration is defined as the weighted mean of the energies of all the multiplets for the designated configuration)[5].

Theory

We used the framework of large unit cell coupled with restricted Hartree – Fock method (LUC- RHF). The Restricted Hartree – Fock (RHF) method uses the linear combination of atomic orbitals (LCAO):

$$\psi_i = \sum_u^m C_{ui} \phi_u \quad (1)$$

Here, $C_{\mu i}$ are the combination coefficients. The determination of the combination coefficients is based on the variational methods in quantum mechanics. The variation of these coefficients leads to a set of algebraic equations which are called Roothan – Hall equations [6].

$$\sum_v (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) C_{vi} = 0. \quad (2)$$

In the above equation $S_{\mu\nu}$ is the overlap integral defined by

$$S_{\mu\nu} = \int \varphi_{\mu}(1)\varphi_{\nu}(1)d\tau_1. \quad (3)$$

is the fock operator matrix given by [7]

$$F_{\mu\nu} = H_{\mu\nu} + \sum P_{\lambda\sigma} [(\mu\nu/\lambda\sigma) - \frac{1}{2}(\mu\lambda/\nu\sigma)]. \quad (4)$$

$H_{\mu\nu}$ is the matrix elements of the core Hamiltonian of a single electron in the field of the nuclei. Its operator representation is given by

$$H_{\mu\nu} = \int \varphi_{\mu}(1)[-\frac{1}{2}\nabla^2 - \sum_A \frac{Z_A}{r}] \varphi_{\nu}(1)d\tau_1. \quad (5)$$

Here Z_A is the charge of nucleus A and the summation is overall nuclei. The density matrix is defined by

$$P_{\mu\nu} = 2 \sum_i^{occ} C_{\mu i}^* C_{\nu i}. \quad (6)$$

The summation is over occupied orbitals only for closed shell systems which are the case in the present work. Two-electron integrals are the most time expensive in the above equations, are defined by

$$(\mu\nu/\lambda\sigma) = \int \int \varphi_{\mu}(1)\varphi_{\nu}(1) \frac{1}{r_{12}} \varphi_{\lambda}(2)\varphi_{\sigma}(2) d\tau_1 d\tau_2. \quad (7)$$

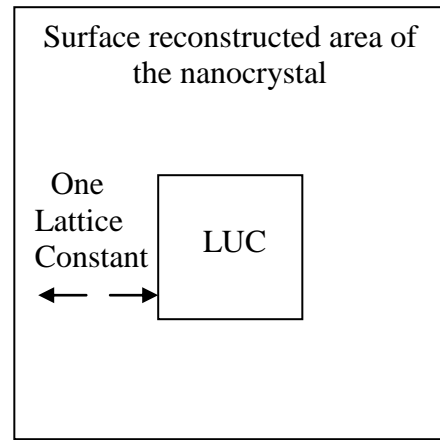
The total energy E^T is defined as

$$E^T = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu} \sum_{\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} [(\mu\nu/\lambda\sigma) - \frac{1}{2}(\mu\lambda/\nu\sigma)] + V_{NN} \quad (8)$$

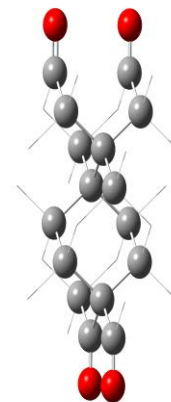
where the last term of the right side of Eq.(8) represents the inter-nuclear potential energy. All the above integrals are evaluated using Gaussian program [3].

In the LUC method, a unit cell that is a multiple of the Bravais cell of Si and Ge structure is used to represent the bulk of crystals [8]. Cells that have diamond structure have integral multiple of lattice constant (a) is multiples of Bravais cell of 8 atoms. Fig.1a shows the geometry of LUC calculations for a nanocrystal, while Fig.1b shows 2D slab calculations of oxygenated 8

atoms of Si and Ge layers the lighted atoms are Si or Ge and the dark upper and lower atoms represent Oxygen atoms. The oxygenated (001)-(1x1) Si and Ge surface is investigated to obtain the total electronic structure of the diamond like structure (Si and Ge) nanocrystal with (001)-(1x1) faces. We used Gaussian 03 program to calculate ab-initio restricted Hartree – Fock electronic structure of diamond nanocrystals internal core. Results of nanocrystals, bulk and surface calculations can be compared with available experimental data of Si and Ge nanocrystals, bulk and surface [9].



(a)



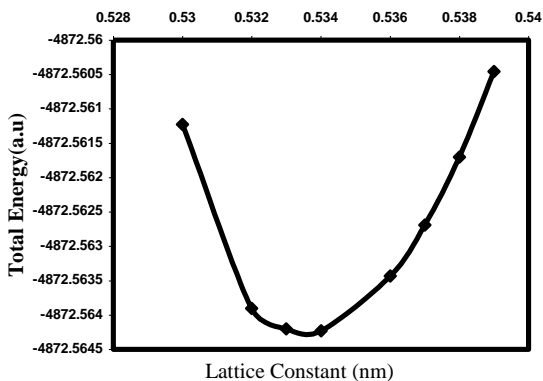
(b)

Fig.1: a- LUC and surface geometry for nanocrystals, b- 2D slab calculations of oxygenated 8 Si and Ge layers.

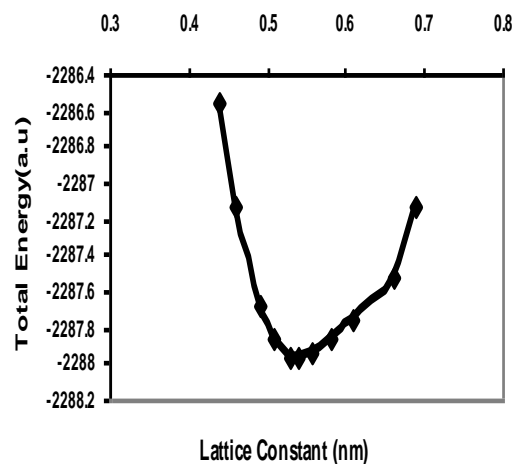
Calculations and Discussion

A LUC of 8 atoms is investigated for Si and Ge nanocrystals. Although this LUC is used typically to simulate bulk materials, we shall investigate the use of this cell to simulate the interior of nanoclusters. The building blocks of this cell is the Bravais unit cells, so that 8

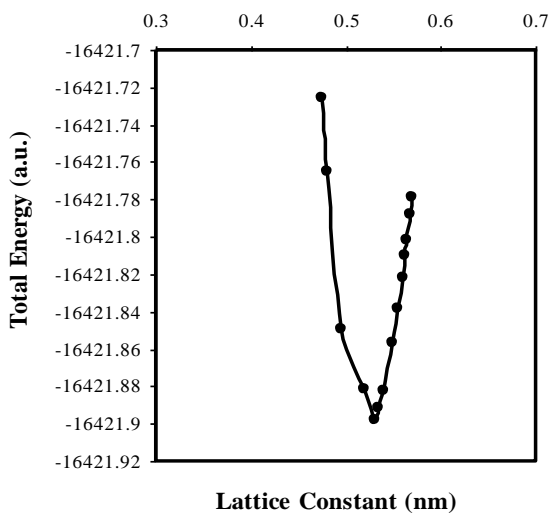
atom LUC refers to one Bravais or conventional diamond unit cell cube with side a (a is the Bravais lattice constant) surrounded by other lattices to passivate outer bonds . Fig (2) shows the total energy as a function of lattice constant for Si and Ge (8 atom LUC core and surface).



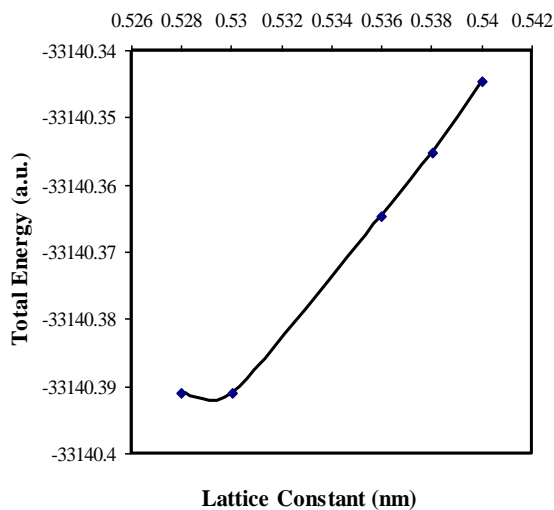
(a)



(b)



(c)



(d)

Fig (2) Total energy (a.u) for 8 atom (LUC), (a) Si surface, (b) Si core , (c) Ge surface and (d) Ge core .

Table (1) gives the electronic structure of the Si and Ge nanocrystals. Cohesive energy, energy gap and valence bandwidth, are obtained from ab-initio calculations.

Experimental lattice constants of bulk (Si & Ge) structure that are used to fit these elements is 0.357 and 0.357 atomic units, for silicon and germanium respectively.

Table (1) Electronic structure of silicon and germanium (core and surface) in comparison with bulk theoretical values [10], (a) electronic structure of Si, (b) electronic structure of Ge.

(a)

| Parameter | Present work | | Bulk theor.[10] |
|------------------------|--------------|------------|-----------------|
| | Si core | Si surface | |
| Cohesive energy(eV) | 7.951 | | 4.721 |
| Energy gap(eV) | 2.763 | 1.383 | 1.151 |
| Valance band width(eV) | 13.650 | 19.337 | 12.432 |
| Lattice constant (nm) | 0.541 | 0.534 | 0.534 |

(b)

| Parameter | Present work | | Bulk theor.[10] |
|------------------------|--------------|------------|-----------------|
| | Ge core | Ge surface | |
| Cohesive energy(eV) | 9.653 | | 3.894 |
| Energy gap(eV) | 2.616 | 0.1953 | 0.969 |
| Valance band width(eV) | 15.841 | 20.414 | 12.923 |
| Lattice constant(nm) | 0.531 | 0.532 | 0.565 |

Density of states as a function of levels energy of 8 atoms LUC, and surface density of states of oxygenated (001)-(1×1)

slab having a² surface area as a function of level energy are shown for Si and Ge in Fig (3) and Fig (4) respectively .

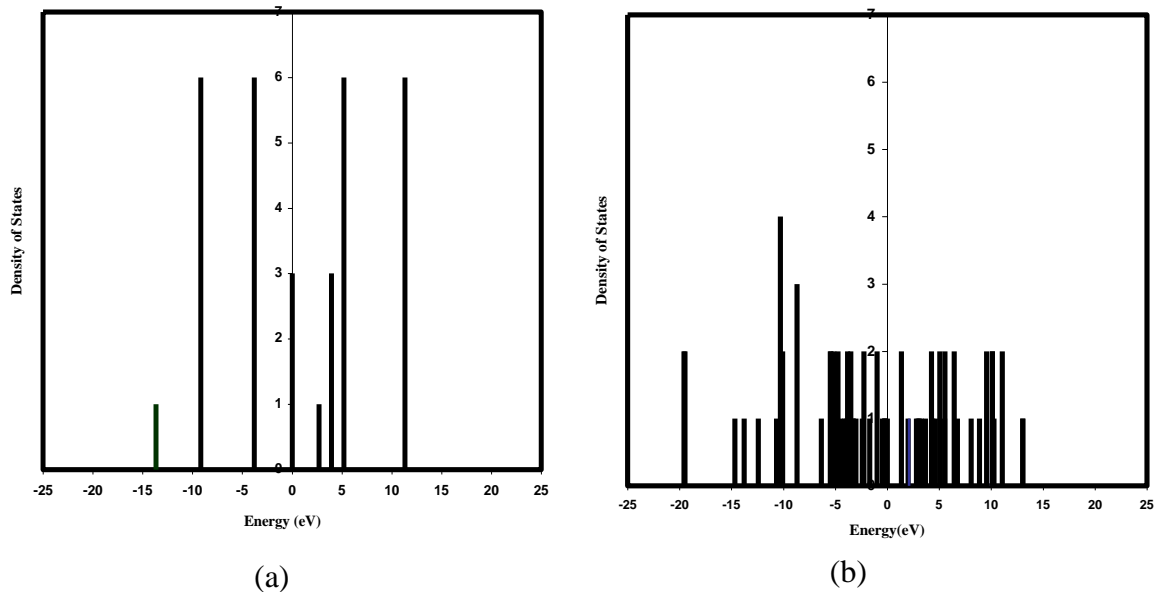


Fig (3) Density of states for Si (8 atoms LUC)as a function of levels energy , (a) density of states for Si nanocrystals core , and (b) surface density of states of oxygenated (001) – (1x1) slab having a^2 area.

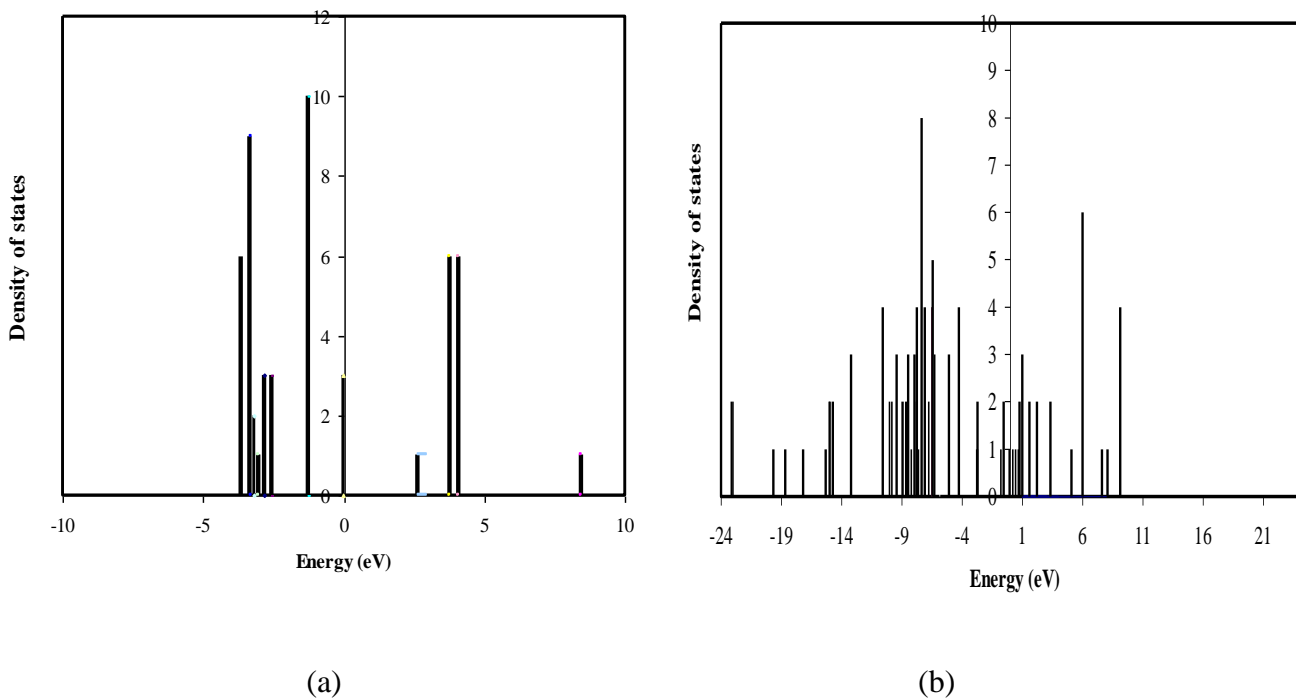


Fig (4) Density of states for Ge (8 atoms LUC) as a function of levels energy , (a) density of states for Ge nanocrystals core , and (b) surface density of states of oxygenated (001) – (1x1) slab having a^2 area.

Relatively lower number of degenerate states is seen in Fig 3b and 4b. This reflects the broken symmetry at the discontinuity at the surface and the existence of new kind of atoms (oxygen atoms), and the variation of bond lengths and angles.

In surface calculations, one can notice that the lattice constant is smaller than in the core in 8 atom calculations, the cell is near the surface in all six directions. The whole nanocrystal in our model is represented by a heterojunction between the surface and the core in which the surface represents the outer most four layers and the core by the rest of the internal region of nanocrystal. The Fermi surface of the two parts should be equalized, however, the valence band maximum of the two parts should also be approximately equal [5, 11]. In both of the two cases, the value of the energy gap is controlled by the surface since this gap is extremely lower for the surface. The matching of the two regions at the junction results in a band bending [5] because of the electric fields [12] and different charges at the two sides of the junction.

Table (1a) shows the parameters for Si and compared with theoretical value, and table (1b) shows the parameters for Ge and compared with theoretical value. Calculations show that the lattice constant and energy gap for Si and Ge nanocrystals surface are smaller than core and bulk lattice constant; In surface calculations, unit lattices that are near to the surface undergo lattice constant expansion in a direction perpendicular to the surface. In 8 atom calculations, the cell is near the surface in all six directions, while the valence band width for the two crystal surface is large than the corresponding value of the core and bulk. Surface discontinuity and oxygen atoms on Si and Ge nanocrystals surface impose level splitting on the highly degenerate bulk diamond structure. This can be seen in Figs

(3,4) when we compare the high number of non-degenerate states in Fig.(3,4)a in comparison with Figs (3,4)b. The splitting does not only affect the number of degenerate states but also the valence band width. The width is wider in surface case. The band gap is also affected by these additional states and splitting as we discussed earlier.

Conclusions

The present calculations show that the energy gap of oxygenated (001)-(1×1) surface decreases in the diamond like nanocrystal surface than the core for both nanocrystals that we investigate (Si and Ge), while the valence band width increases. This indicates a cut off of the quantum confinement region in which the energy gap decreases continuously. Experimentally and theoretically this cut off of the quantum confinement is reported previously. The surface layers of Si and Ge nanocrystals contain different and varying structures ranging from minimally reconstructed to a distorted diamond structure depending on passivating atoms and kinetics of the reconstruction processes. The dangling bonds or oxygenated surfaces have strong effects on the electronic structure including the energy gap.

The present method can be used to simulate nanowires or nanofilms by elongating one or two of the coordinates of the cluster to be larger than the others. These calculations can be performed if the smallest dimensions of these nanostructures are larger than the threshold length to create a well established diamond structure core. Similar calculations of the present work can also be found when simulating a composite material that contains diamond structure core that is surrounded by amorphous carbon.

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