First-Principles Calculations on Cohesive Energy of Bulk and Nano Si

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ABSTRUCT - The structure properties in the pseudopotential density-functional scheme were investigated using Ab initio pseudopotential method within both local density approximation (LDA) and generalize gradient approximation (GGA) for silicon bulk and nanoscale solids. The calculated bulk lattice constant of silicon is found to match with experimental data from both LDA and GGA, whereas the bulk cohesive energies obtained from GGA are much closer to the experimental data than that from LDA. The cohesive energies for silicon nanoparticles, nanowires and nanofilms diverts from that of the bulk when particle sizes decreases. At size of 4 nm, the cohesive energy value of nanoparticles is -3.477 eV, which is larger than that of nanowires -4.116 eV and nanofilms -4.514 eV. The results obtained are in good agreement with literature data.

Index Term – Ab-initio calculation, Density Functional Theory, Electronic Structure, Nanocrystals, Lattice constant, Cohesive Energy and Si.

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1   Introduction

Nanocrystals are under considerable investigation worldwide because of their wide scientific and technological interest. Thanks for the unique properties of nanocrystals, the fabrication of nanostructure materials and nanodevices with desirable properties in atomic scale has become an emerging interdisciplinary field involving solid-state physics, materials science, chemistry and biology [1]. Silicon material is the leading semiconductor material and dominates current industry. The application of silicon nanocrystaline particles has become an extensive and attractive area of research due to their diverse properties [2]. Silicon nanoparticles, known as one of the most important types of nanomaterials, feature a number of unique merits, such as excellent electronic, optical, thermodynamic properties, huge surface-to-volume ratios, and facile surface modification [3-6].

The cohesive energy as an important physical quantity is often strongly connected to the unique properties of nanostructures [7]. The cohesive energy of solid can be measured experimentally by determining the heat of sublimation [8] or computed by theoretical methods such as density functional theory (DFT) [9], cellular method [10], KKR method [11], linear muffin-tin orbital method [12] and many other ones. All of them are developed for calculating the cohesive energy of bulk materials. It has been reported that the cohesive energies measured for both Mo and W of nanoparticles are strongly depend on their size which was carried out by Kim *et al.* [13]. Currently there are several detailed theoretical models available for determining cohesive energy of nanoparticles which are applied for metals. Jiang and his colleges [14] reported a model based on thermodynamical analysis and employed well on nanoscale size dependence of solids. Fang *et al.* [15] have used a Molecular Dynamic (MD) simulations based on the Stilling-Weber potential model to calculate cohesive energy for silicon nanoparticles, while Maeda *et al.* [16] have used the total energy calculation based on a Transferable-Tight-Binding (TB) model for silicon nanowires.

The first-principle calculations of material properties, relying upon quantum mechanics and electromagnetism has undergone tremendous

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progress. Density Functional Theory (DFT) is at the heart of this rapid evolutio. The difficulty of fully solving the Schrödinger equation for the wave function has been solved by Kohn-Sham [9, 17], who showed that the task of finding the right electron density can be expressed in a way that involves solving a set of equations in which each equations only involves a single electron. The Kohn-Sham equations represent a mapping of the interacting many-body system onto a system of non-interacting electron moving in an effective potential due to all the other electrons. Furthermore, DFT in the Kohn-Sham implementation with LDA [17] or GGA [18] approximation for the exchange-correlation functional has been successfully applied to deduce structure, electronic, magnetic as well as other properties of myriad of condense matter systems[19].

In the present work, the cohesive energy based on the first-principles density functional theory calculations is investigated for bulk silicon as a standard and nanocrystals in a size range from 2 to 19 nm. The results are analyzed and compared with literature data.

2   Theoretical Method:

2.1 Computational Details:

In order to find out the electronic structure and the properties of matter, the time-independent Schrödinger equation must be solved. In this work, the total energy self-consistently by means of first principles electronic structure is performed within LDA using the Perdew-Wang [20] and GGA using the Perdew-Burke-Ernzerh [21] at the Kohn-Sham DFT level. The Ab-initio DFT calculations are performed by using the ABINIT code [22] which is based on the plane-wave basis set. Ultrasoft Troullier-Martin [23] pseudopotential was used to describe the interactions of ionic and valance electrons. In addition, to accurately approximate integrals over the Brillion zone calculations of the electronic states over special sets of k points, Monkhorst and pack [24] uniform set for any crystal was used.

The code has several input parameters or variables some of which should be optimized that gives ground state total energy. The convergence

of the system should be checked with respect to the total energy as a function of both cut-off energy and total number of k points for the plane wave expansion of the wave functions before any calculations such as electronic properties, geometry optimization etc. Different cut-off energies were tested (between 2 to 40 Hartree) and the cut-off energy of (30 Hartree) was found to achieve better convergence within both LDA and GGA. Also, according to the Monkhorest Pack scheme the Brillion zone was sampled. To get high degree of convergence, the grid size from (2×2×2) to (14×14×14) k-points were tested and (12×12×12) mesh was used to achieve better convergence for both silicon Bulk and nanocrystals. In all cases, the energy convergence was achieved with the tolerant on the difference of a total energy of less than 5×10^{-7} eV.

On the other hand, the total energy of an isolated Si atom is needed for evaluating the cohesive energy. The total energy of an isolate Si atom was calculated with a super cell geometry based on DFT implemented in the ABINIT code. A Si atom supposed to be in the center of a huge periodically repeating unit cell. Calculations concerning isolate energy were performed in the cubic cell size (45Å×45Å×45Å) with cut-off energy of (30 Hartree) to the energy convergence of less than 1×10^{-11} eV within both LDA and GGA.

2.2 Lattice Constant and Cohesive Energy for Si Bulk and its Nanoscale size:

The model for calculating size dependent lattice constant in bulk and nanoscale size, respectively is reported by Omar [25] as follow:

$$a(\infty) = \frac{4}{\sqrt{3}} d_{mean}(\infty) \tag{1}$$

and

$$a(r) = \frac{4}{\sqrt{3}} d_{mean}(r) \tag{2}$$

where (∞) and (r) refers to bulk and nanosize. Then $a(\infty)$ and $a(r)$ are the bulk and nanocrystals unit cell lattice constant and d_{mean} is the lattice mean bond length. The size dependent mean bond length $d_{mean}(r)$ is calculated according to the following relation;

$$d_{mean}(r) = h - \Delta d_{mean}(r) \qquad (3)$$

where h is the first surface layer inter-planer distance of the crystal. This value for silicon is 0.3368nm, $\Delta d_{mean}(r)$ which is the increase in mean bond length is calculated according to [26]:

$$\Delta d_{mean}(r) = \Delta d_{mean}(r_c) \left[e^{\frac{-(\beta-1)}{(\frac{r}{r_o}-1)}} \right]^{\frac{1}{2}} \qquad (4)$$

For $\Delta d_{mean}(r_c)$ as the maximum increase in the mean bond length as $d_{mean}(r_c) = h - \Delta d_{mean}(r_c)$ and is equal to 0.0988 nm, β as a related material constant is 2.5 for silicon [25], r is the radius of the nanoparticles and r_o denotes a critical radius at which all atoms of the particle are located on the bulk surface and is calculated from $r_o = (3 - d)h$. In this equation, d = 0 for nanoparticles (NPs) where r has a usual meaning of radius, d = 1 for nanowires (NWs) where r being taken as its radius and d = 2 for nanofilms (NFs) with r denoted its half thickness [27, 28].

The cohesive energy is an important physical quantity that accounts for the bond strength of a solid, which equals the energy needed to divide the solid into isolated atoms by breaking all the bonds. Cohesive energy is also a basic quantity for thermodynamics, by which almost all thermodynamic properties of materials can derive [8]. Consider the unit cell of N atoms; the bulk cohesive energy $E_{coh}(\infty)$ per unit cell is [29, 30]:

$$E_{coh}(\infty) = \frac{E_{tot}(\infty) - \sum_N E_{iso}}{N} \qquad (5)$$

where E_{iso} is the energy of an isolated atom. In this work, Eq.(5) is modified for applications on nanoscale size material for both LDA and GGA as follow;

$$E_{coh}^{LDA,GGA}(r) = \frac{E_{tot}^{LDA,GGA}(r) - \sum_N E_{iso}^{LDA,GGA}}{N} \qquad (6)$$

3 Results and Discussion:

A series of lattice constants $a(\infty)$ have been taken to calculate the total energies $E_{tot}(\infty)$ as illustrated in Fig. (1) and Fig. (2). In order to increase the speed of the calculations, the process was carried out on the primitive cell rather than the conventional cell. The equilibrium lattice constant value calculated for silicon bulk structure are in better agreement for both LDA (5.424 Å) and GGA (5.463 Å) compared to reported experimental data as shown in Table (1). Calculations in light of equations from (1) to (4) give an increase to the lattice constant from 5.431Å for bulk to 6.632Å, 6.144Å and 5.751Å with 2nm for nanoparticles, nanowires and nanofilms respectively. These results were used to calculate the modified minimum total energy as well as cohesive energy for nanoparticles, nanowires and nanofilms. The data within GGA shows that the absolute values of minimum total energy $E_{tot}^{GGA}(r)$ are strongly depends on the nanoscale size. They decreases from (-214.463 eV) for bulk state to minimum values of (-212.157 eV), (-213.435 eV) and (-214.231eV) at r = 2nm for three different dimension. Since $d_{mean}(r)$ for a nanoparticle (NPs) has large size dependence, then it has less total energy compared to both nanowires (NWs) and nanofilms (NFs) as seen in Fig. (3). On the other hand, it has been explained that, increase in bond energy due to the size reduction of nanocrystals is from the surface coordination imperfection formation. In metal, this induces atomic lattice contraction on the nanoparticles surface and that strengthening of remnant lattice bonds [31, 32, 33]. In case of Si, Ma *et al.* [34] reports a 12% contraction in Si-Si surface bonds with the decrease in nanowires diameter from 7 to 1.3 nm.

Through Eq. 5, the cohesive energies $E_{coh}(\infty)$ were obtained by taking the energy difference between atomic equilibrium energy in the silicon structure and the energy of isolated atoms. According to the data listed in Table (1), the cohesive energy obtained from GGA has better values in comparison to the experimental one (4.63eV), that is why the method is chosen for the size dependence parameters in this work. The size-dependent cohesive energies for nanocrystals within GGA $E_{coh}^{GGA}(r)$ were calculated by taking the obtained minimum values of $E_{tot}^{GGA}(r)$ due to Eq. (6) and the dependence is shown in Fig. 4. The increase of mean bond length leads to decrease in

cohesive energy with the decrease of nanosize in this figure. Note that in the center of nanocrystals the bond length is almost the same as it is for the bulk, which gives the bulk cohesive energy. For smaller sizes where atoms at surface layers have larger percentage of the total number of atoms in nanocrystals considered, the cohesive energy value is smaller. At 4 nm sizes, $E_{coh}(r)$ reduces by 25%, 11% and 2.5% for NPs, NWs and NFs respectively. The present calculation values on cohesive energy of Si nanoparticles have the same trend variation in comparison with the reported experimental results for Mo and W nanoparticles [13] thier absolute values of $E_{coh}(r)$ decreases with the size reductions.

Furthermore, the results obtained in the present work for $E_{coh}^{GGA}(r)$ are in good agreement with those reported using MD [15] and TB [16]. The variation in the cohesive energies has the same size dependent trend when r > 6nm for NPs and r > 5nm for NWs. While for smaller r, MD and TB give lower values. The higher deviation dependence in the lower scale is expected to be related to the size dependence of lattice constants applied in this work. When particle sizes decrease to several nanometers the bond length stretches larger than that of bulk silicon and then the total energy decreases which is lead to decrease the cohesive energy as shown in Fig. (4).
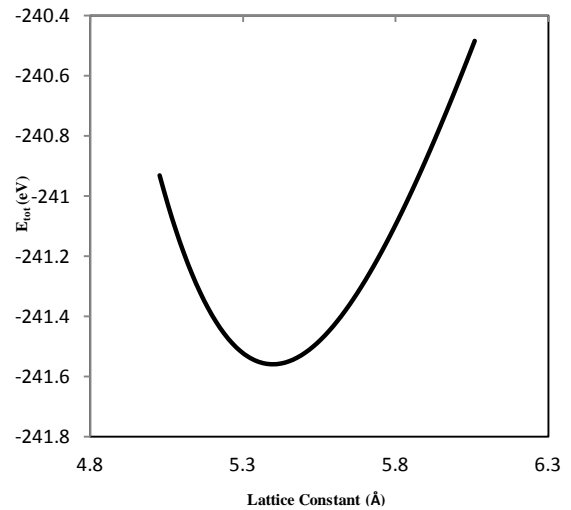

Fig.(1): Total energy versus lattice constant for Bulk Si within LDA.
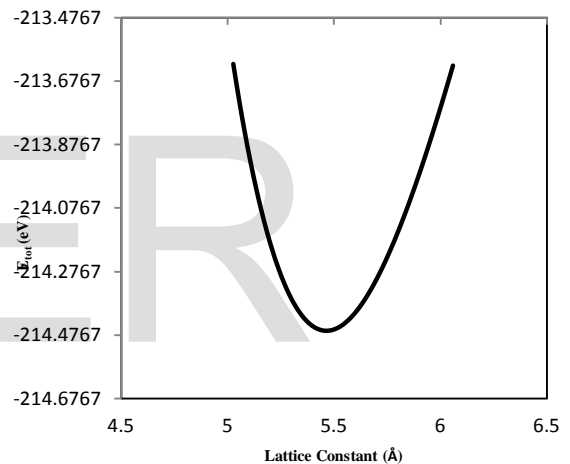

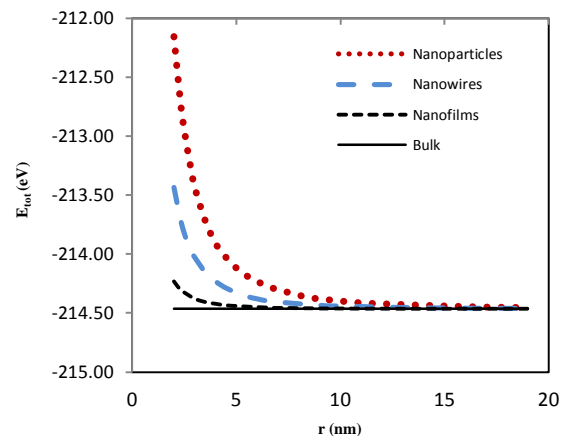**Fig.(2):** Total energy versus lattice constant for Bulk Si within GGA.

Fig.(3): The difference between the minimum total energies as a function of radius for various nanocrystals within GGA.
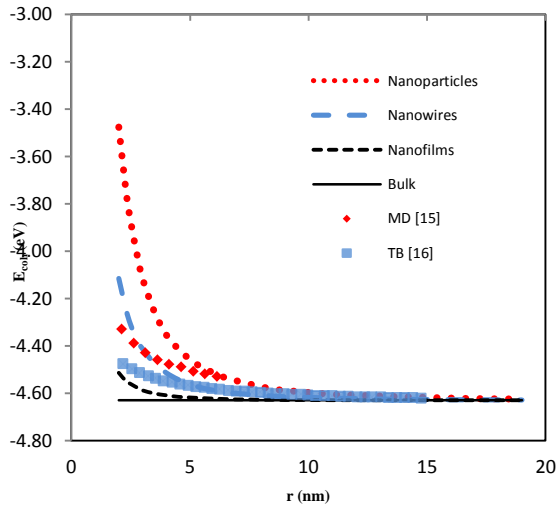
Table (1): The calculated and experimental equilibrium structural properties of bulk Si within LDA and GGA and percentage error are given in parentheses for this work:

Structural Properties	This Work		Other Theoretical Works Employed (LDA & GGA)	Exp. Data
	LDA	GGA		
a(∞) (Å)	5.424 (0.13%)	5.463 (0.58%)	(5.378,5.463)[29], (5.390,5.460)[35], (5.488,5.490)[36], (5.407,5.475)[37], (5.403,5.466)[38]	5.431[3]
$E_{tot}(\infty)$ (eV)	-241.555	-214.463		
E_{iso} (eV)	-115.118	-102.206		
$E_{coh}(\infty)$ (eV)	-5.66 (18.19%)	-5.02 (7.76%)	(-6.00, -5.42)[29], (-5.37,- 4.44)[35], (-4.30 Employed MD)[15], (-4.50 Employed TB)[16]	-4.63[40]

Fig.(4): Nanoscale size dependence cohesive energy for Si.

4 Conclusions:

Using first-principles calculations based on DFT within GGA, we studied the cohesive energy of bulk Si as well as that of nanocrystals. The size dependence of mean bond length explains well the cohesive energies for all nanostructured types. The absolute values of $E_{coh}(r)$ decreases with the decrease of nanoscale size and the effects are stronger for nanoparticles than that of both nanowires and nanofilms.

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