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Dimer interactions of magic $W@Si_{12}$ clusters

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Abstract

Design of stable Si-cage and Si-tube structures is of great importance to the fields of Si nanotechnology and microelectronics. In order to explore the possibility of constructing a Si nanotube by using the metal-stabilized and tube-shaped Si cluster $W@Si_{12}$ as the basic unit, detailed first-principles calculations are performed to analyse the interactions of the dimers. It is found that the interactions are orientation dependent, and no interactions exist if stacking is along the sixfold axis. However, the W atom can be used as the spacer to link two units, resulting in a metastable structure. Due to the large surface stress in such a small one-dimensional system, sixfold stacking cannot be extended, and thus the trimer is not dynamically stable. Further, the most stable geometry for the dimer is seriously distorted. Consequently, it is difficult to construct a Si nanotube using this $W@Si_{12}$ tube-shaped unit.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Silicon offers many potential applications including computer chips, micro-electronic devices, chemical catalysts and new superconducting compounds. There is an impetus, however, to increase the flexibility of its sp^3 bonding and create the variety of structures already produced with carbon, including C_{60} [1] and nanotubes [2]. There are currently two main directions in this search for new Si structures:

- (1) to design a Si cluster with a fullerene cage structure;
- (2) to create a one-dimensional Si structure such as a nanotube.

The Si nanowire has attracted a great deal of attention [3–6] due to its important applications in microelectronics. Such interest has arisen because the electronic properties of carbon nanotubes are sensitively dependent on their helical symmetry and diameter, resulting in semiconducting or metallic electronic properties that can influence the field emission behaviour of the tubes. The conductivity of silicon nanowires, though, is not sensitive to its morphology or dimensions. Furthermore, we know that the first, second and third ionization potentials (IPs) of the Si atom are 8.5, 16.3 and 33.5 eV, much smaller than those of the

Table 1. Ground- and excited-state configurations and expectation values of S^2 (an indicator of spin contamination) for the W atom using a number of functionals and basis sets: LanL2DZ [10, 11] and SDD [8]. The resulting values of the promotion energy, Δ , should be compared with the experimental value of 0.18 eV [12].

E_{xc}	Basis set	Ground state $5d^56s^1$			Excited state $5d^46s^2$			Δ
		Spin up	Spin down	$\langle S^2 \rangle$	Spin up	Spin down	$\langle S^2 \rangle$	
B3LYP	LanL2DZ	$5d^56s^1$	$5d^06s^0$	12.0002	$5d^46s^1$	$5d^{0.2}6s^{0.98}$	6.0005	0.2083
B3LYP	SDD	$5d^56s^1$	$5d^06s^0$	12.0006	$5d^46s^1$	$5d^{0.2}6s^{0.98}$	6.0007	0.2867
B3PW91	LanL2DZ	$5d^56s^1$	$5d^06s^0$	12.0004	$5d^46s^1$	$5d^{0.03}6s^{0.96}$	6.0011	0.8541
B3PW91	SDD	$5d^56s^1$	$5d^06s^0$	12.0014	$5d^46s^1$	$5d^{0.03}6s^{0.96}$	6.0110	0.9207
BPW91	LanL2DZ	$5d^56s^1$	$5d^06s^0$	12.0002	$5d^46s^1$	$5d^{0.05}6s^{0.95}$	6.0011	0.9552
BPW91	SDD	$5d^56s^1$	$5d^06s^0$	12.0004	$5d^46s^1$	$5d^{0.05}6s^{0.95}$	6.0011	0.9988

C atom (11.3, 24.4 and 47.9 eV). Therefore, it can be expected that there are some potential advantages for Si nanowires over the carbon tubes in field emission and other applications of microelectronics.

Recently the Si_{12}W cluster, the geometry structure of which is a hexagonal-shaped tube [7], was found experimentally to be magic and stable. This elegant structure is composed of two hexagonal rings with a W atom in its centre. Is it possible to use this tubelike cluster as a building block to construct a one-dimensional structure such as a nanowire? In this paper, we study the dimer interactions for the magic W@Si_{12} cluster, which is the first step in constructing a Si nanowire with this cluster as its basic unit.

2. Computational method

Ab initio methods based on density-functional theory (DFT) are well established tools to study the structural properties of materials. We have used molecular orbital theory in which the cluster wavefunction is represented by a linear combination of atomic orbitals centred at each atomic site. The Gaussian98 package [8] was used and calculations were performed at the B3LYP level of theory [9] with the LanL2DZ effective core potential basis set [10, 11]. The applicability of the basis set and the exchange–correlation functional was examined from the promotion energy of the W atom from the ground to the excited state, as shown in table 1, where the values of $\langle S^2 \rangle$ rule out spin contamination in our calculations. Compared with the experimental value of 0.18 eV for the promotion energy of the W atom [12], the hybrid exchange–correlation functional B3LYP together with the LanL2DZ basis set behaves much better than the other choices, as is also true for the IP and electron affinity (EA) of the Si atom. In our calculations, the atomic positions were relaxed without symmetry constraint, and the optimization was terminated when all the forces acting on the atoms were less than $0.001 \text{ eV \AA}^{-1}$.

3. Results and discussion

Before discussing dimer interactions, we first examine the monomer. For W@Si_{12} , we start with ten different initial structures, and the equilibrium geometry is found to be a hexagonal-shaped tube with D_{6h} symmetry, in agreement with the previous study [7]. Figure 1(a) shows the optimized structures together with the vibrational frequency spectra, where the arrows on the frequency spectra specify the vibrational modes with large contributions from the W atom.

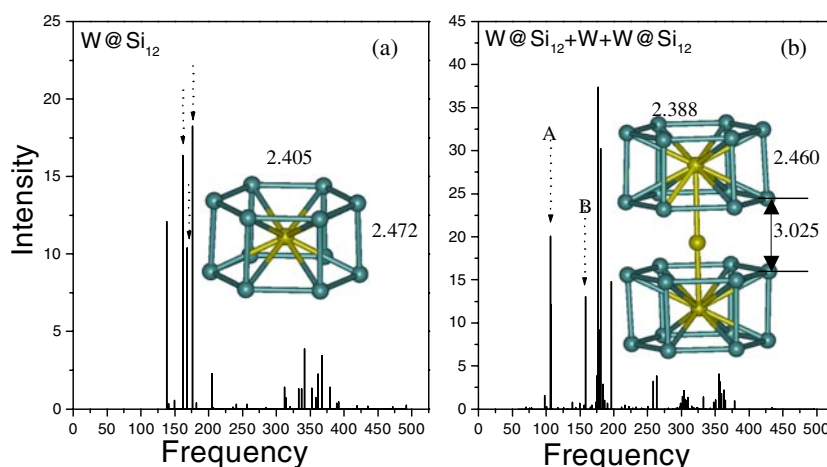


Figure 1. Geometry and vibrational spectra for W@Si₁₂ and the linked 6–6 configuration of the dimer. The frequency is in cm⁻¹, and the IR intensity is in km mol⁻¹.

We can see that all frequencies are real, verifying the dynamical stability of this geometry. The HOMO–LUMO gap is 2.60 eV, much larger than the previous one of 1.18 eV [7]. This difference can be explained from the addition of a small amount of exact exchange in the exchange–correlation functional, which has been shown in other systems to dramatically improve the HOMO–LUMO gap with respect to experiment [13]. If the same exchange–correlation potential (BPW91) is used as in [7], the gap is 1.22 eV; however, the functional also fails to describe the promotion energy of W, as indicated in table 1. The ground state of the cluster is a singlet, and energies of +1.255, +2.580 and +4.035 eV are found for spin states with multiplicities of three, five and seven. There is a charge transfer of 3.18 electrons from the Si cage to the W atom.

Because the W@Si₁₂ cluster is not spherical in geometry, its interactions should be orientation dependent. There are two typical high-symmetry axes: the sixfold axis (through two hexagons) and the twofold axis (through the two opposite squares). Thus, for geometry optimization of the dimer we consider the following possibilities, as shown in figure 2.

- (1) Stacking of the two clusters through the sixfold axis (labelled as the 6–6 configuration). After optimization, the two clusters fly apart, the distance between the two units increasing to 6.30 Å. The same result is also found when one cluster is rotated through 30° relative to the other about the sixfold axis (the *R*-6–6 configuration).
- (2) Stacking of the two clusters through the twofold axis (the 2–2 configuration). The interaction energy is found to be 0.937 eV, and for a 45° rotation about the twofold axis, the interaction energy increases to 1.036 eV (the *R*-2–2 configuration).
- (3) Stacking of the two clusters through the sixfold axis in one cluster and the twofold axis in the other (the 6–2 configuration).

The resulting interaction energy is found to be 1.079 eV. We can see from figure 2 that although the structure of the W@Si₁₂ cluster itself is quite beautiful, the most stable structure for the dimer is seriously distorted.

Why do the two clusters repel each other when stacked along the sixfold axis? We know that the HOMO and LUMO are important for the interaction; the effective overlap between the HOMO in one cluster and the LUMO in another cluster can result in a stronger interaction.

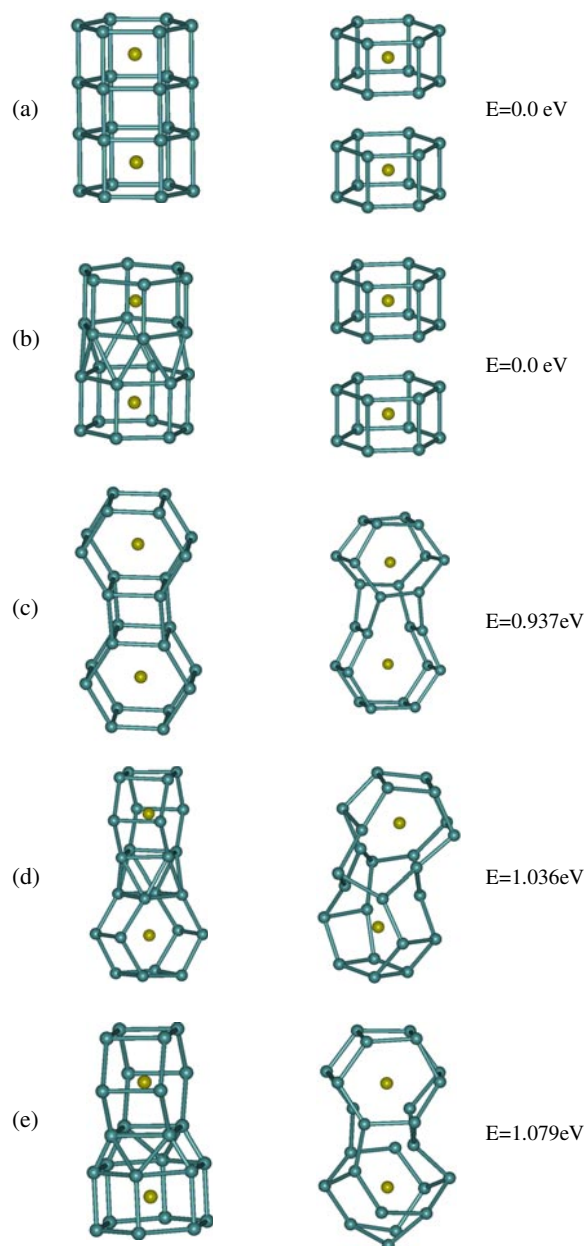


Figure 2. Five possible $W@Si_{12}$ dimer configurations: (a) 6–6, (b) *R*-6–6, (c) 2–2, (d) *R*-2–2, and (e) 2–6.

However, we found that the HOMO and LUMO in the $W@Si_{12}$ cluster are mainly localized on the W atom, which is inside the cluster. In order to have a good overlap of the HOMO and LUMO, the two clusters must be very close to each other. On the other hand, due to the charge transfer from Si to W, the Si atoms are positively charged; a short distance will produce a large Coulomb repulsion, which is strongest for stacking along the sixfold axis among all the configurations. Therefore, they cannot bind each other.

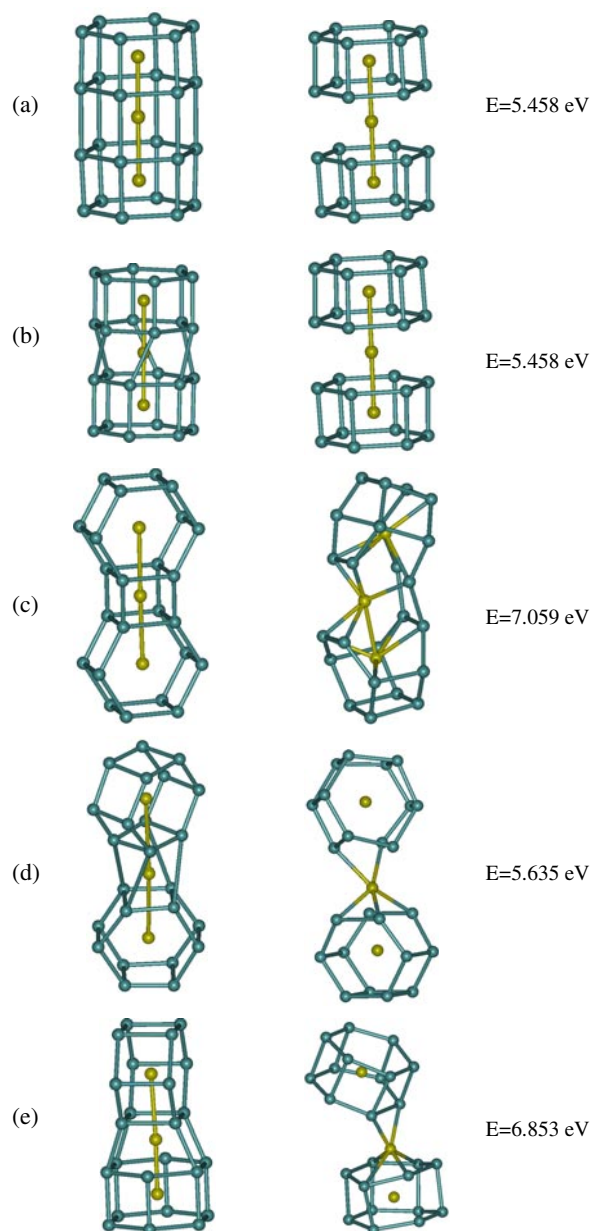


Figure 3. Five possible geometries for $W@Si_{12} + W + W@Si_{12}$, where the W atom is used as a spacer to link the two units: (a) 6-6, (b) R-6-6, (c) 2-2, (d) R-2-2 and (e) 2-6.

Can we find a spacer that would link the two units? Due to the hexagonal shape of $W@Si_{12}$, from the geometrical point of view we have two candidates for such a spacer: benzene (C_6H_6) and Si_6H_{12} , the latter of which is also found to be stable experimentally [14, 15]. However, after full optimization, we found that neither of the two spacers can successfully link the two units. Finally, because the W atom can link two six-member Si rings, we tried W as a spacer. We found that the beautiful ring structure is maintained in the final geometry, and it is also dynamically stable. Figure 1(b) shows the frequency spectrum, where the main contributor to

vibrational mode A is the W spacer atom, and the main contributors to vibrational mode B are the other two W atoms inside the tube-shaped units. The nearest distance between W atoms is 2.766 Å. Compared with the isolated unit, the structure for the linked dimer becomes more compact; the two W atoms are not in the centres of the units, but are shifted outwards to the ends, and more charge is transferred to the W atoms from Si, where the linking W atom receives 1.62 electrons, and the other two W atoms receive 3.25 electrons. Due to the dimerization, the HOMO–LUMO gap is reduced to 1.44 eV. When one of the two clusters is rotated through 30° relative to the other about the sixfold axis (*R*-6–6 configuration), the final structure is restored to the configuration shown in figure 1(b), which shows that the structure is stable against relative rotations. The distance between the two units is 3.025 Å. The energy decrease for this link (the link energy) is 5.458 eV. We studied the other three possible configurations as mentioned above to determine which structure is most stable. The link energies are 7.059, 5.635 and 6.853 eV for the 2–2, *R*-2–2 and 2–6 configurations, respectively. Thus, in the case of linked clusters, the most stable geometry is the 4–4 configuration with a seriously distorted final structure, as shown in figure 3. The 6–6 configuration is a metastable state; however, if we link the third unit to this configuration, the geometry becomes dynamically unstable. Because the linked dimer itself is just metastable, adding another unit is equivalent to applying some perturbation, which drives the geometry to a more stable one, so we can conclude that a tubelike Si nanowire is difficult to construct from the W@Si₁₂ tubelike unit.

In summary, detailed studies are presented for W@Si₁₂ and its dimer. Compared with the previous study, we found that the B3LYP functional is more suitable to describe the energies of the system. The dimer interactions are orientation dependent. In contrast to the case of carbon, where very flexible bonding features exist and single, double and triple bonds can easily be formed, the larger number of core electrons in Si makes it much more difficult for two Si atoms to form double or triple bonds. Consequently, Si prefers to form multidirectional single bonds (sp³), which makes construction of a tubelike Si nanowire difficult even when using the W@Si₁₂ tubelike unit.

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