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Electronic properties of transition-metal-atom doped Si cage clusters*

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Abstract. We present a density-functional study of electronic structures of convex-caged Si clusters doped with transition-metal (TM) atoms. First, we show the reason for their peculiar geometries in terms of interplay among the electron orbitals of Si and TM atoms. Then we describe the potential ability of the clusters to serve as charge sources to other objects such as Si crystal surfaces.

PACS. 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 36.40.Cg Electronic and magnetic properties of clusters

1 Introduction

Modern electronic device technology has been ready for mass production of silicon (Si)-based metal-oxide-semiconductor (MOS) field-effect transistors (FET's) with physical gate lengths being only 50 nanometers [1]. Further miniaturization of devices would continue and require more sophisticated technologies to accurately process materials in several nanometers or even smaller length scales. Constructing silicon (Si) clusters that contain roughly 10–1000 atoms may be one of very important subjects to fertilize useful techniques for that purpose. In order to maximize the controllability of the clusters, it is essential that they have simple and well-defined structures. However, the energetically favorable structures of *pure* Si_n (n up to $\sim$20) clusters are rather complicated [2]. It is also hard to understand intuitively the reason for the stability of their structures, too.

Inspired by the work by Beck [3], we have so far clarified in previous studies that silicon clusters may have hollow cage structures if certain transition-metal atoms are incorporated in the clusters [4–6] and also that those cages have well-defined topologies modeled as convex simple 3-polytopes, the numbers of whose inner diagonals passing close to the metal atoms are maximized [7,8].

There have been some theoretical studies of metal-atom encapsulated Si and Ge clusters [9–14]. In most of them, however, sufficient care has not been paid to searching for lowest-possible energy structures of the clusters. Instead, the authors of those studies have just presented results of local optimizations in the vicinity of a few initial structures they assumed. They have not given substantial explanations for why the cluster structures they have obtained are energetically favorable. In contrast, we have attempted a serious search for the global-energy-minimum structures of WSi_n clusters in recent studies [7,8].

The purpose of this presentation is twofold. First, we describe the electronic structures of WSi_{12} and WSi_{14} clusters obtained previously [7,8] to demonstrate how it is much easier to understand the atomic structures of these clusters than *pure* silicon clusters. Second, we present chemical potentials and hardnesses of some TM-atom-doped Si clusters, $M\mathrm{Si}_n$, ($M = \mathrm{W}$, Re, Ta, Nb, $n = 12$, 14 and 16). Based on the latter result, we will argue the ability of the Si clusters with TM atoms behaving as charge sources to other macroscopic bodies such as semiconductor surfaces.

2 Method of calculation

We have defined a two-step strategy to obtain low-energy structures of WSi_n clusters. In the first step, we have performed genetic-like structure updates of the clusters. This corresponds to a global search of potential energy minima. As for the genetic-like operations, we have adopted the single-parent evolution algorithm (SPEA [15]). In this step, each cluster may experience several energy minima, finally approaching the lowest-possible-energy minimum given by each SPEA run. In the second, a local optimization around the selected minimum has been done by using a quenched molecular dynamics method. In both steps,

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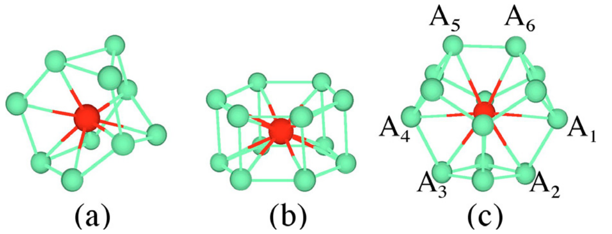

Fig. 1. (Color) Lowest-energy structures of (a) WSi_{10}, (b) WSi_{12} and (c) WSi_{14} clusters found in our calculation. Pale grey (green) and dark grey (red) balls represent Si and W atoms, respectively. The line segments connecting any pair of atoms are drawn when the inter-atom distance is less than 2.7 Å. In panel (c), the six Si atoms of the cluster are labeled as A_i $(1 \leq i \leq 6)$.

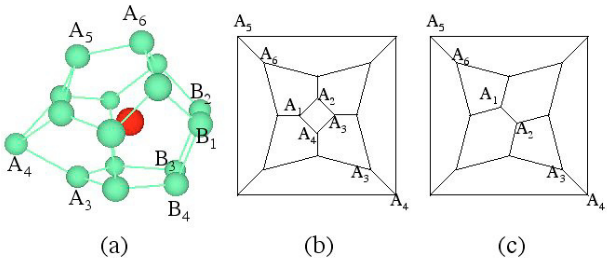

Fig. 2. (Color) (a) A structure of the WSi_{16} cluster recently found in our calculation. The conventions are the same as those in Figure 1. It should be noted that the distances from W and all Si atoms are larger than 2.7 Å. Schlegel diagrams of the Si cage structures of WSi_{16} (panel (a)) and WSi_{14} (Fig. 1c) are shown in panels (b) and (c), respectively. See also Figure 4 of reference [17].

estimation of the total energy has been performed with density-functional theory within the generalized gradient approximation. In principle, one wish to use simple analytical potential functions or tight-binding parameters for the total energies calculated in step (1) to find as many local minima as possible. However, we do not know any such formulas whose accuracy to describe the interactions between Si and W atoms has been established. This is why we had to use density-functional theory in step (1) as well as (2), limiting the number of sampled potential-energy surfaces in step (1). Thus we do not insist at present that the lowest-energy structures of WSi_n clusters that we show are of real global energy minima [16].

For evaluation of chemical potential and chemical hardness, we have performed local optimization of the structures of $M\mathrm{Si}_n$, $M\mathrm{Si}_n^+$ and $M\mathrm{Si}_n^-$ clusters, each starting from the counterpart of WSi_n.

3 Results

3.1 Atomic structures

First we review the geometry of the WSi_n clusters. Figure 1 shows optimized structures of WSi_{10}, WSi_{12} and WSi_{14} clusters whose respective energies are found to be lowest in our calculation. As already pointed out [7,8], well-defined cages occur for a certain range of the number of Si atoms, 12 (Fig. 1b) and 14 (Fig. 1c). The topology of these cages are identified to be that of the convex simple 3-polytope where the number of inner diagonals [17] close to the W atom is maximized. Our structure of WSi_{14} is different from that reported by Kumar and Kawazoe [14,18]. The structure of the WSi_{10} cluster (Fig. 1a) is not a cage of the same kind as WSi_{12} and WSi_{14} clusters, although the ten Si atoms do surround the W atom.

We have reported previously [7,8] that the arrangement of Si atoms in the WSi_{16} cluster does not have a cage of convex simple 3-polytope but appears to be either the cage of WSi_{12} (Fig. 1b) or WSi_{14} (Fig. 1c) where either four or two Si atoms are attached, respectively. The structures have been obtained by local optimizations for the initial cage structures configured in the 16-vertex convex simple 3-polytopes. Based on this result, we have concluded that there should be a finite range of the cluster size for which convex Si cages are favored.

Very recently, we have found using our full SPEA-based structure optimization that the WSi_{16} cluster may also have a hollow cage structure that may be modelled as the 16-vertex convex simple 3-polytope with the maximum number of the inner diagonals (Fig. 2a). This is the same as that reported by Kumar and Kawazoe [14]. However, the actual cage shape is not convex, suggesting that formation of a convex Si cage is not energetically favorable for $n = 16$. In addition, the structure of the obtained WSi_{16} cluster in Figure 2a can be configured by attaching two additional Si atoms to the cage of the WSi_{14} (Fig. 1c). This result originates from the fact that the topology of the cage in Figure 2a is closely related to that of Figure 1c so that one of Si "dimers" (atom pair A_1 and A_2, for example; see Figs. 1c and 2c) is just replaced by a "tetramer" (B_1, B_2, B_3 and B_4, see Fig. 2b). Further, the distances between the W atom and Si atoms are all longer than 2.7 Å at variance with WSi_{12} and WSi_{14}, suggesting that the W-Si-cage bonding is weaker than that in the WSi_{12} and WSi_{14} clusters. All these features of the result shown in Figure 2 imply that the cage with sixteen Si atoms in a convex simple 3-polytope is too large and unfavorable to form to surround a W atom, supporting the existence of the "magic number" for n of WSi_n as described in the above paragraph.

In order to understand the peculiar geometries of WSi_{12} (Fig. 1b) and WSi_{14} (Fig. 1c), it is useful to illustrate wavefunctions contributing to W-Si bonds. In the case of WSi_{12} (Fig. 3), there are twelve molecular orbitals bridging the W- and Si-atom sites. These orbitals are mainly composed of W d orbitals with a small amount of s counterpart and s- or p-dominant orbitals at each Si atom. As is obvious in Figure 3, symmetry of the W d orbitals is very favorable for the Si cage in a regular hexagonal prism structure. As for WSi_{14} (Fig. 1c), there are fifteen molecular orbitals (not shown in this paper) with similar characters to those shown in Figure 3 for WSi_{12}. These results justify to approximate the W-Si bonds with inner diagonals of each Si cage passing close to the W atom, establishing a clear identification of the

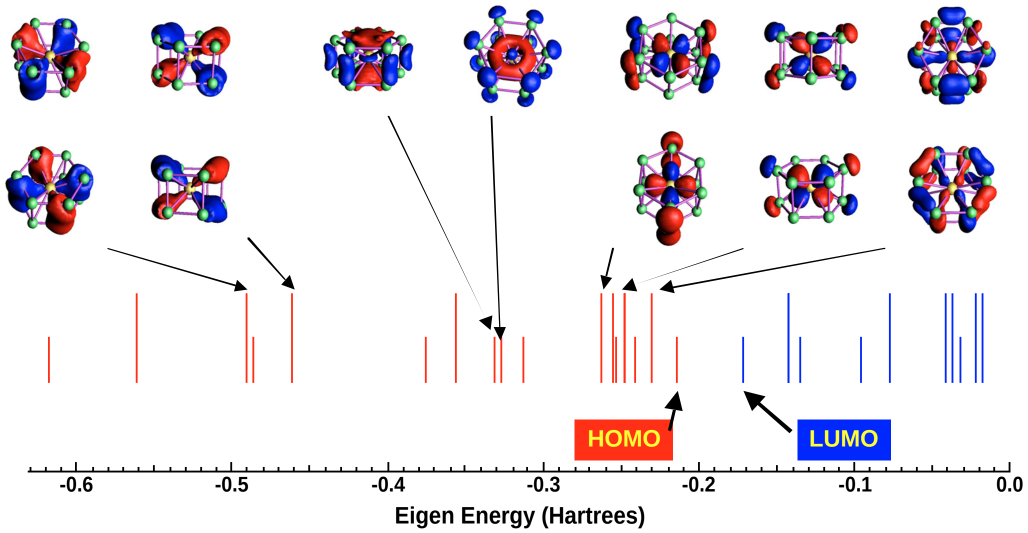

Fig. 3. (Color) Wavefunctions contributing to the W-Si-cage bonds of the WSi_{12} cluster. Grey (red) and black (blue) lobes illustrate wavefunctions with opposite phases. Distribution of the eigenvalues is also shown. The positions of grey (red) and black (blue) bars correspond to occupied and unoccupied eigenstates, respectively. The length of each bar represents degeneracy of the eigenstate (single or doubly degenerate).

essence of the Si cage structures in WSi_{12} and WSi_{14}, the magic-number clusters of WSi_n, in terms of topology [7,8].

3.2 Chemical potential and chemical hardness

For estimation of the potential ability of TM-atom doped Si clusters as charge sources to other macroscopic bodies, it may be a first-step study to calculate their IP's (I) and EA's (A). In practice, we discuss their chemical potentials (μ) and chemical hardnesses (η) instead [19]. Let us denote the total energy of an N-electron system as $E(N)$. Then, for $\varDelta N \ll N$, we have

$$E(N+\varDelta N) \simeq E(N) + \left.\frac{\mathrm{d}E}{\mathrm{d}x}\right|_{x=N} \varDelta N + \frac{1}{2}\left.\frac{\mathrm{d}^2E}{\mathrm{d}x^2}\right|_{x=N} (\varDelta N)^2. \tag{1}$$

The μ and η are defined as

$$\mu \equiv \left.\frac{\mathrm{d}E}{\mathrm{d}x}\right|_{x=N} \tag{2}$$

and

$$\eta \equiv \frac{1}{2}\left.\frac{\mathrm{d}^2E}{\mathrm{d}x^2}\right|_{x=N} = \frac{1}{2}\left.\frac{\mathrm{d}\mu}{\mathrm{d}x}\right|_{x=N}. \tag{3}$$

Since $I \equiv E(N-1) - E(N)$ and $A \equiv E(N) - E(N+1)$, and setting $\varDelta N = 1$, μ and η are related to I and A *via*

$$\mu = -\frac{I+A}{2} \tag{4}$$

and

$$\eta = \frac{I-A}{2}. \tag{5}$$

Consider two systems with μ_i and η_i ($i = 1, 2$) contacting each other, where some amount of electron charges ($\varDelta M$) transfers from one to another. Let us determine $\varDelta M$ and the resultant energy change ($\varDelta E$) due to the charge transfer [20]. The total energies after charge transfer are

$$E_1(N_1 + \varDelta M) \simeq E_1(N_1) + \mu_1 \varDelta M + \eta_1 (\varDelta M)^2 \tag{6}$$

and

$$E_2(N_2 - \varDelta M) \simeq E_2(N_2) - \mu_2 \varDelta M + \eta_2 (\varDelta M)^2. \tag{7}$$

Correspondingly, chemical potentials become

$$\mu_1' = \left.\frac{\mathrm{d}E_1(x+\varDelta M)}{\mathrm{d}x}\right|_{x=N_1} \simeq \mu_1 + 2\eta_1 \varDelta M \tag{8}$$

and

$$\mu_2' = \left.\frac{\mathrm{d}E_2(x-\varDelta M)}{\mathrm{d}x}\right|_{x=N_2} \simeq \mu_2 - 2\eta_2 \varDelta M, \tag{9}$$

to first order in $\varDelta M$ after the charge transfer. Establishment of chemical equilibrium after charge transfer requires $\mu_1' = \mu_2'$, from which we find

$$\varDelta M \simeq \frac{\mu_2 - \mu_1}{2(\eta_1 + \eta_2)}, \tag{10}$$

$$\varDelta E \simeq -\frac{(\mu_1 - \mu_2)^2}{4(\eta_1 + \eta_2)}. \tag{11}$$

Note that, in equation (11), $\varDelta E$ is the energy gain of the total system (1+2) due solely to the alignment of the chemical potentials of the two systems at the same value. There may be an additional energy gain provided by Coulomb attraction between the two, if the initial states of the both were charge neutral. It is evident from equations (10, 11) that a guiding principle to predict the occurrence of an easier charge transfer is a large difference in μ together with low η_1 and η_2.

Table 1. Preliminary results for the electronic properties of TM-atom encapsulated Si clusters. I, A, μ and η denote ionization potential, electron affinity, chemical potential and chemical hardness, respectively. For the relationship between (I, A) and (μ, η), see equations (4, 5) in the text.

Cluster	I (eV)	A (eV)	μ (eV)	η (eV)	μ/η
$NbSi_{12}$	7.544	3.955	–5.750	1.795	–3.104
$NbSi_{14}$	7.272	3.785	–5.528	1.744	–3.170
$NbSi_{16}$	6.066	3.237	–4.651	1.415	–3.287
$TaSi_{12}$	7.632	4.060	–5.846	1.786	–3.273
$TaSi_{14}$	7.257	3.756	–5.507	1.751	–3.145
$TaSi_{16}$	7.014	3.663	–5.338	1.676	–3.185
WSi_{12}	7.586	2.965	–5.275	2.311	–2.283
WSi_{14}	7.100	3.027	–5.064	2.037	–2.486
WSi_{16}	6.922	2.890	–4.906	2.106	–2.330
$ReSi_{12}$	7.395	2.362	–4.878	2.517	–1.938
$ReSi_{16}$	6.212	2.900	–4.556	1.656	–2.751

Keeping the preliminaries above in mind, we have calculated chemical potentials (μ) and chemical hardnesses (η) for some metal-encapsulated Si clusters (Tab. 1). For this purpose, we have performed local optimization of the structures of a neutral cluster and ions with ±1 charge for each $M\mathrm{Si}_n$, starting from the optimized structure of neutral WSi_n. We have run the Gaussian98 [22] code to do this job, where the effective core potentials [23] were used to model the Coulomb interactions between the valence electrons and the atomic cores, and the Becke'88 [24] and Perdew-Wang'91 [25] functionals were adopted for exchange and correlation energies, respectively. Evaluating the μ/η ratio to search for a cluster with a high ability to accept an electron with a low chemical hardness, we find $TaSi_{12}$ and $NbSi_{16}$ clusters to have the large $|\mu/\eta|$ ratios. The $TaSi_{12}$ cluster meets these two conditions, whose electron affinity (4.060 eV) is outstandingly high. Considering also the low chemical hardness (see Eqs. (10, 11)), one can expect that the $TaSi_{12}$ cluster may serve as a charge-transfer-type *acceptor* to other substances, such as Si crystals. More detailed assessment of the ability of the charge transfer doping with TM-atom encapsulating Si clusters is now underway. The high potential ability of this cluster to be an acceptor is greatly suppressed by attaching one more Si atom to generate a $TaSi_{13}$ cluster. This result means that the electronic properties of TM-atom-doped Si cage clusters are rather sensitive to the parity of the number of Si atoms.

4 Conclusion

We have presented electronic properties of TM-atom-doped Si cage clusters. Based on calculated chemical potentials and hardnesses of some clusters we have shown a first-approximation picture of the potential ability for the clusters to become sources of charges, especially the agents for charge-transfer-type doping.

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