

A form of bulk silicon consisting of “magic” clusters

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Si₄ clusters are soft-landed on an inert Van-der-Waals surface and the island formation is studied using x-ray and ultraviolet photoelectron spectroscopy. The experimental data indicate that the clusters do not fuse to Si islands but survive as individuals. The potential-energy surface of two Si clusters is calculated and a barrier against fusion is found, in agreement with the experiments. Both findings support the existence of a form of silicon consisting of Si₄ clusters.

Since the discovery of the “supermagic” cluster C₆₀¹ the possibility of the synthesis of new materials consisting of stable clusters fascinates researchers. In case of C₆₀ and similar fullerenes like La@C₈₂, such materials exist and fullerite—the bulk material formed by weakly interacting C₆₀ “soccer balls”—represents a new form of carbon.²

The question arises, whether magic clusters of other elements like Si or Al might be suitable as building blocks of cluster materials. However, many of these clusters are more reactive compared to the fullerenes, and the chemical methods² used for the separation of fullerene materials cannot be used for clusters of most other elements. In experimental studies of free clusters many other stable clusters have been found, such as C₃₂³ or Si₄.^{4,5} In addition, there are predictions of possible building blocks of new materials like Al₁₃H^{6,7} and Si₄₅.⁸

For the studies published so far, relative stability is the only criterion making a cluster a candidate as a building block for new material. However, even more important is the interaction between neighboring clusters. In cluster materials neighboring clusters “touch” each other, and there must be a barrier against fusion.

Here we present combined experimental and theoretical results on the interaction between neighboring magic clusters. As a first example, magic Si₄ clusters are selected. Experimentally, the clusters are mass-selected and soft landed on an inert surface.⁹ They are highly mobile on this surface at room temperature and will form islands of bulk Si if there is no barrier.^{10–12} The samples are studied using x-ray and ultraviolet photoelectron spectroscopy (XPS, UPS) and, in contrast to an earlier study of Si₁₀ on amorphous carbon,¹³ the spectra contradict the formation of islands, supporting the existence of a barrier. The interaction potential between two approaching Si₄ clusters is calculated for two geometries, and for both channels a barrier is found. Accordingly, a new bulk consisting of Si₄ clusters should exist.

Density functional calculations for the Si₄ clusters have been performed with the gradient-corrected exchange-correlation (xc) functionals of Perdew, Burke and Ernzerhof

(PBE).¹⁴ The computational details are similar to the studies of Au,^{15–19} modified to the case of Si.²⁰

In a first step, the ground state structure of a Si₄ cluster was determined. The Si₄ cluster forms a planar rhombohedral structure with two sharp and two flat corners. Fixing the distance R between two Si atomic centers on the x -axis in two different Si₄ clusters, the potential energy surface was

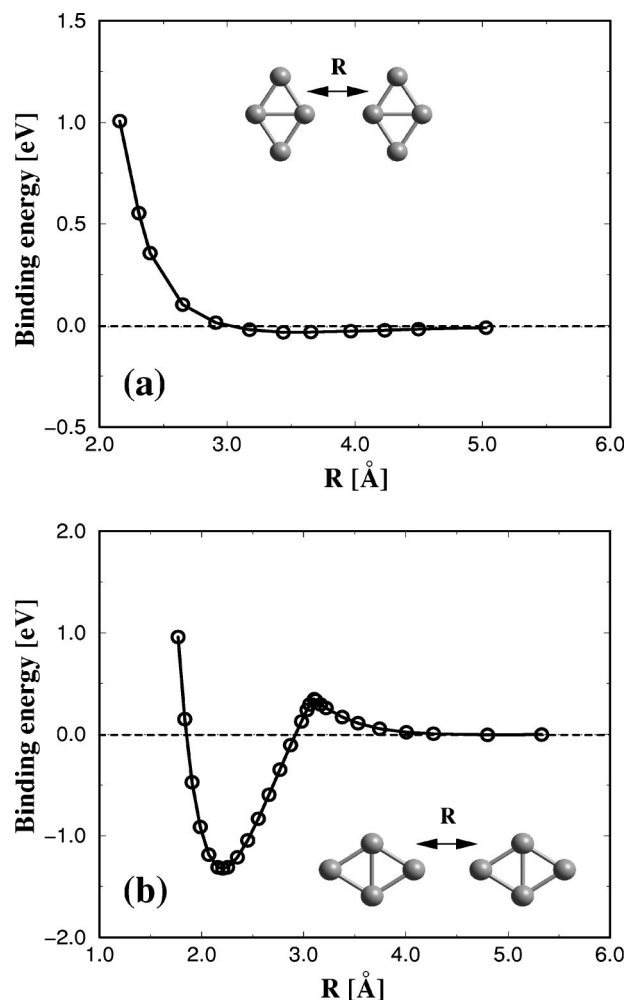


FIG. 1. Calculated potential energy curves for two neutral interacting Si₄ clusters. Two different reaction channels have been calculated: the two tetramers approaching each other with the flat (a) and sharp (b) corners ahead. Case (a) is repulsive, while in case (b) a bond is formed. In (b) an energy barrier is observed at a distance of 3.1 Å and a height of 0.3 eV.

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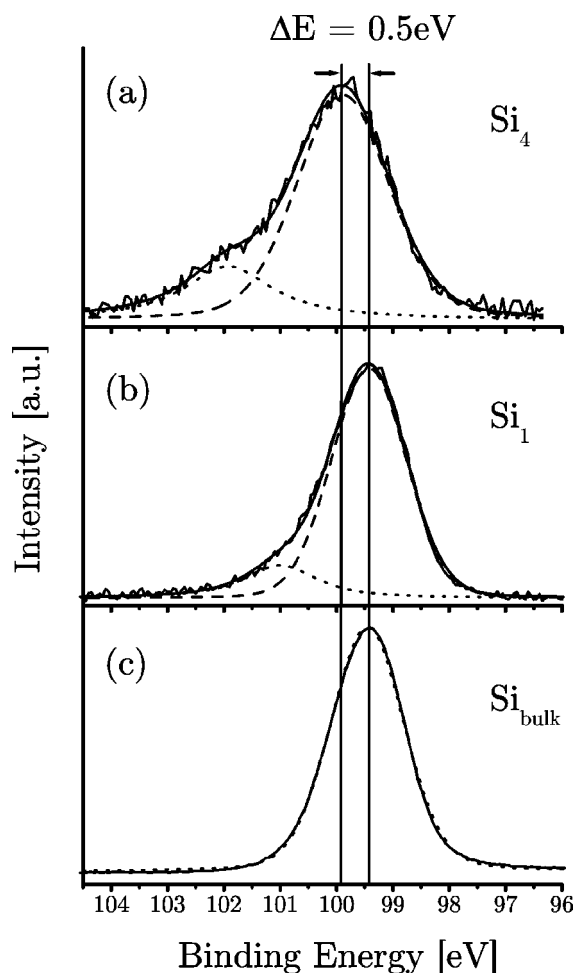


FIG. 2. XPS spectra of the Si 2p peak recorded for (a) Si_4 clusters deposited at 5 eV onto HOPG (2% coverage), (b) positively charged Si atoms deposited at 5 eV onto HOPG (2% coverage) and (c) for a Si bulk reference sample. Fits of the experimental data are also displayed.

calculated. Two different “reaction channels” have been considered (see Fig. 1) starting with structures with symmetry about the x -axis. In Fig. 1(a) the distance between the two Si atoms at the fla angles is fixed and in Fig. 1(b) the distance of the atoms at the sharp angles is fixed. The total energy is displayed in Fig. 1 as a function of R .

The experimental setup has been described in detail elsewhere.⁹ In short, cluster ions are generated using a cluster ion source and mass separated. The ions are decelerated down to a kinetic energy of 1.2 eV/atom and landed on highly oriented pyrolytic graphite (HOPG). The sticking coefficient is only about 10%,²¹ and a coverage of 2% of Si atom monolayer (ML) has been achieved after 2 h. There is no generation of surface defects at this low kinetic energy.^{9–12} We can not exclude cluster fragmentation, but it seems unlikely at this low kinetic energy compared to the binding energy of the clusters.^{9,12} The clusters on the surfaces are studied using XPS and UPS *in situ*.^{9,11,22,23}

Figure 1 displays the calculated dependencies of potential energy of two interacting Si_4 as a function of distance. There are several geometries possible for two tetramers approaching each other. We assume the Si_4 clusters lie fla on the surface and, therefore, we are restricted to planar geometry of two Si_4 approaching each other with the two obtuse (a) or sharp (b) corners encountering one another. For the

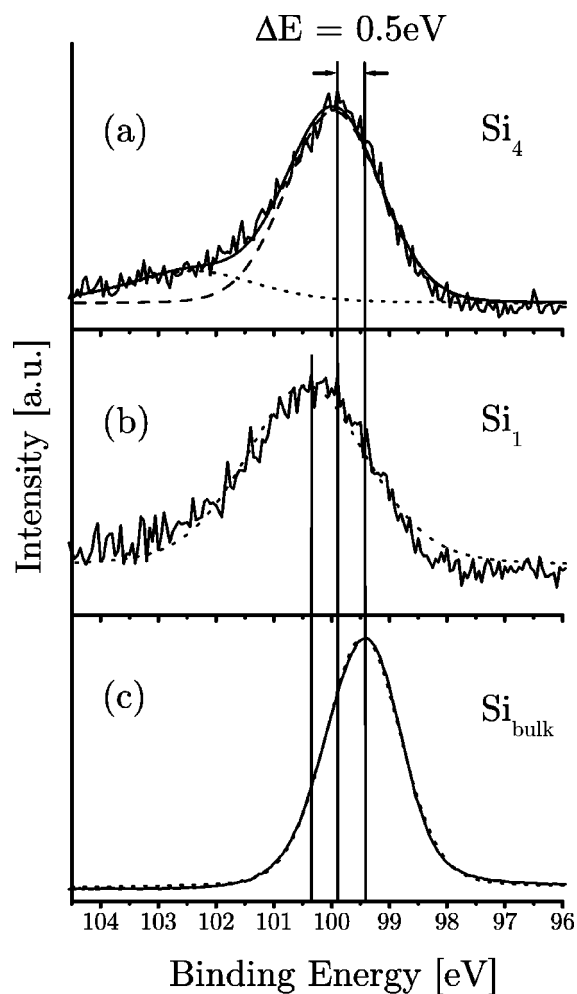


FIG. 3. XPS spectra of the Si 2p feature recorded for (a) Si_4 clusters deposited at 5 eV onto amorphous carbon (4% coverage), (b) positively charged Si atoms deposited at 5 eV onto amorphous carbon (3% coverage) and (c) for a Si bulk reference sample.

geometry displayed in Fig. 1(a) the potential energy corresponds to a repulsive interaction. If the two Si_4 approach with the sharp corners ahead a bond is formed [Fig. 1(b)] with a binding energy of 1.3 eV.

Important in Fig. 1(b) is the small increase of the potential energy at a distance of 3.1 Å. This barrier is 0.3 eV high and, therefore, it might not be overcome at kinetic energies corresponding to room temperature. Accordingly, for both channels a repulsive interaction at low temperatures is predicted.

These theoretical findings support the results of an experimental study of Si_4 clusters deposited on HOPG at room temperature. We assume that the interaction with the substrate is weak and no change of the structure of the Si_4 is to be expected. The clusters most likely lie fla on the surface, are highly mobile at room temperature and approach each other in geometries similar to the ones calculated. The samples are studied using XPS and only the peak corresponding to the 2p core level of Si is examined (Fig. 2). For clean bulk Si an almost symmetric peak centered at a binding energy of 99.4 eV is observed [Fig. 2(c)]. For Si atom ions on HOPG [Fig. 2(b)] a similar peak is observed with a shoulder corresponding to a feature at 101 eV binding energy. For Si_4 clusters on HOPG [Fig. 2(a)] a shift of the main peak of

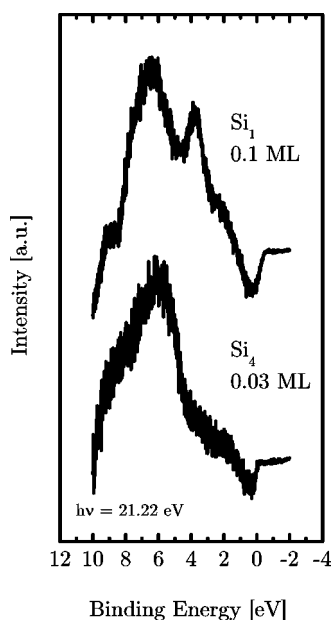


FIG. 4. UPS ($h\nu=21.22$ eV) data of deposited Si_1^+ ions (10% coverage) and Si_4^- cluster anions (3% coverage) on amorphous carbon at room temperature. The data have been obtained by subtracting the spectrum of the clean carbon substrate from the spectrum of the substrate with the Si atoms or clusters deposited.

0.5 eV towards higher binding energy and a shoulder corresponding to a peak around 102 eV is observed.

The small features at binding energies around 101–102 eV are assigned to Si bound to carbon. The main peak corresponds to Si bound to Si. The shift of 0.5 eV between the deposited clusters and the deposited atoms is essential. We explain this shift by a lower average coordination number of the Si atoms in clusters. Similar shifts have been observed in XPS spectra of various mass-selected deposited clusters.^{11,13,22,23} In these experiments the clusters are not mobile on the surface^{13,22} or, if the clusters can diffuse, the shift vanishes with time due to the formation of bulk-like islands.¹¹ In our case the clusters are mobile,^{9,11} but the shift does not vanish with time. In case of the deposited atoms there is no shift corresponding to the formation of bulk-like islands. These findings indicate that deposited Si_4 clusters do not form larger islands, but remain as individual clusters on the surface.

To support our findings we repeated the above experiments with amorphous carbon. This surface has a high number of dangling carbon bonds. Figure 3 displays the XPS data. For the deposition of Si atom ions [Fig. 3(b)], almost no pure Si–Si bonds, but only Si atoms bound to carbon are found. No Si islands are formed, but the Si atoms are trapped at surface defects.

In contrast, the XPS feature corresponding to the soft landed Si_4 cluster ions [Fig. 3(a)] does not exhibit a difference to the case of the HOPG surface [Fig. 2(a)]. The tetramers do not react with defect sites of the amorphous carbon and do not coalesce.

For further support we studied the samples with UPS. At the photon energy used here ($h\nu=21.22$ eV) the cross section for photoemission from silicon is rather low and we did not succeed in obtaining UPS data for HOPG substrates. Figure 4 displays a comparison of UPS data of Si atoms and

Si_4 clusters on amorphous carbon. The data correspond to the difference between the UPS spectra of the sample with clusters and the clean sample. In both spectra a broad peak at 6–7 eV binding energy is observed, which can be assigned to Si-derived valence orbitals. For the deposited atoms, an additional peak at 4 eV is observed, which we tentatively assign to the formation of Si–C, in agreement with the XPS data (Fig. 3). The Si_4 sample does not exhibit such a feature. Both the XPS and UPS data for amorphous carbon show that the Si_4 clusters are rather inert.

In conclusion, we studied the interaction of neighboring Si_4 clusters theoretically and experimentally. Both sets of data support the idea that this magic silicon cluster is suitable as a building block for a new cluster material. In the calculations, a repulsive barrier has been found in the interaction potential that blocks spontaneous fusion of clusters at sufficiently low temperature. Experimentally, for clusters deposited on an inert surface at room temperature, no tendency to form larger islands of bulk Si is observed.

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