

RZ 3405 (# 93505) 02/25/02
Mathematics & Physics 6 pages

Research Report

A New Form of Bulk Silicon Consisting of “Magic” Clusters?

M. Grass¹, D. Fischer^{1,2}, M. Mathes¹, G. Ganteför¹ and P. Nielaba¹

¹Department of Physics
University of Konstanz
D-78457 Konstanz
Germany

²IBM Research
Zurich Research Laboratory
8803 Rüschlikon
Switzerland

LIMITED DISTRIBUTION NOTICE

This report has been submitted for publication outside of IBM and will probably be copyrighted if accepted for publication. It has been issued as a Research Report for early dissemination of its contents. In view of the transfer of copyright to the outside publisher, its distribution outside of IBM prior to publication should be limited to peer communications and specific requests. After outside publication, requests should be filled only by reprints or legally obtained copies of the article (e.g., payment of royalties). Some reports are available at <http://domino.watson.ibm.com/library/Cyberdig.nsf/home>.

IBM Research
Almaden · Austin · Beijing · Delhi · Haifa · T.J. Watson · Tokyo · Zurich

A New Form of Bulk Silicon Consisting of “Magic” Clusters?

M. Grass¹, D. Fischer^{1,2}, M. Mathes¹, G. Ganteför¹ and P. Nielaba¹

¹*Department of Physics, University of Konstanz, D-78457 Konstanz, Germany*

²*IBM Research, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland*

Abstract

The question, whether stable “magic” silicon clusters are suitable as building blocks for new cluster materials is examined. Si₄ clusters are soft-landed on an inert Van-der-Waals surface and the island formation is studied using x-ray photoelectron spectroscopy (XPS). The XPS 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 new form of silicon consisting of Si₄ clusters.

Since the discovery of the “supermagic” cluster C_{60} [1] the possibility of the synthesis of new materials consisting of highly stable clusters fascinates many researchers. In case of C_{60} and similar fullerenes like C_{70} and $La@C_{82}$ such materials exist and, e.g., fullerite — the bulk material formed by weakly interacting C_{60} “soccer balls” — represents a new form of carbon beside diamond and graphite [2]. This discovery triggered a revolution of research in carbon based materials.

The question arises, whether “magic” clusters of other elements like Si or Al might be suitable as building blocks of new cluster materials. However, many of these clusters are much more reactive compared to the rather inert fullerenes and the chemical methods [2] which were used for the generation and separation of fullerene materials cannot be used for clusters of most other elements. In experimental studies of free clusters in the gas phase many other very stable clusters have been found like C_{32} [3] or Si_4 [4,5]. In addition, there are also theoretical predictions of possible building blocks of new materials like e.g. $Al_{13}H$ [6,7] and Si_{45} [8].

For the theoretical and experimental studies published so far the relative stability is the only criterion making a “magic” cluster to a candidate as building block for new cluster 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. This is, e.g., the case for two C_{60} . C_{120} is much more stable than two weakly interacting C_{60} [2], but the two C_{60} do not fuse at room temperature.

Here, for the first time we present combined experimental and theoretical results on the interaction between neighboring “magic” clusters. As a first example, magic Si_4 clusters are selected. Experimentally, the clusters are mass-selected and soft landed on an inert van-der-Waals surface [9]. They are probably highly mobile on this surface at room temperature and will immediately form large islands of bulk Si if there wouldn’t be a barrier against fusion [10–12]. The samples are studied using XPS and, in contrast to an earlier study of Si_{10} on amorphous carbon [13], the spectra contradict the formation of large islands supporting the existence of a barrier. Theoretically, the interaction potential between two approaching Si_4 clusters is calculated for two geometries and for both channels a barrier against fusion is found which is large compared to room temperature. Accordingly, a new bulk of pure Si consisting of Si_4 clusters should be existing. And even more general, if this is true for some magic silicon clusters it might also be true for many other clusters found to be stable in the gas phase.

The density functional (DFT) calculations for the Si_4 clusters have been performed with the approximative gradient-corrected exchange-correlation (xc) functionals of Perdew, Burke and Ernzerhof (PBE) [14]. This choice for the xc-functional should give reliable results whenever both localized and extended electron states appear. The computational details are similar as in the studies of Au [15–19], modified to the case of Si [20].

In a first step the ground state structure of an isolated Si_4 cluster was determined. The isolated Si_4 clusters form planar rhomboedric structures with two sharp and two flat corners. Fixing the distance R between two Si- atomic centers on the x -axis in two different Si_4 - clusters the potential energy surface was calculated. In this procedure all particle coordinates were fixed to a plane initially — approximating the geometrical constraint for the clusters induced by the surface — and then full structural relaxation of the clusters in three spatial dimensions was allowed. 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 flat angles is fixed, in Fig. 1(b) the distance of the atoms at the sharp angles. The total energy is displayed in Fig. 1 as a function of R . These calculations correspond to the situation of the clusters in the gas phase. However, since the interaction to the Van-der-Waals surface is small the results obtained can be considered a good approximation to the case of deposited clusters.

The experimental set up has been described in detail elsewhere [9]. In short, cluster ions are generated using a pulsed arc cluster ion source (PACIS) and mass separated with a 45° sector magnet. The ions are decelerated down to a kinetic energy of 5 eV (1.2 eV/atom for Si_4) and soft-landed on highly oriented pyrolytic graphite (HOPG). The HOPG samples are prepared by cleavage in air and heating in vacuum at 500°C for 1 h. Ion currents of up to 2nA for Si_4 were obtained. The sticking coefficient is only about 10% [21] and a coverage corresponding to about 2% of Si atom monolayer (ML) has been achieved after 2h of deposition. There is no generation of surface defects at this relatively low kinetic energy as examined using scanning tunneling microscopy [9–12]. We can not totally exclude cluster fragmentation but seems unlikely at this low kinetic energy compared to the binding energy of the clusters [9,12]. Great care has been taken to minimize influences of residual gases like hydrocarbons, which might contaminate the surface during cluster deposition. The clusters on the surfaces are studied using x-ray photoelectron spectroscopy (XPS) “in situ” [9,11,22,23] at room temperature.

Fig. 1 displays the calculated dependencies of potential energy of two interacting Si_4 clusters as a function of distance. The corresponding geometries are shown in the inserts. Neutral Si_4 in its electronic ground state is a planar rhombus and there are several geometries possible for two tetramers approaching each other. We assume the Si_4 clusters lie flat on the surface and, therefore, we restricted to planar geometry of two Si_4 approaching each other with the two obtuse (a) or sharp (b) corners encountering. For the geometry displayed in Fig. 1a the potential energy increases monotonously with decreasing distance corresponding to a repulsive interaction. The two clusters do not fuse. If the two Si_4 approach with the sharp corners ahead a bond is formed (Fig. 1b). A minimum with a binding energy of 1.3eV is calculated corresponding to the formation of a Si_8 cluster. The geometry corresponding to this minimum does not correspond to the equilibrium geometry of a Si_8 [20,24] cluster (in fact it is 2.7 eV higher in energy) and represents a metastable isomer.

The large differences between the two geometries displayed in Fig. 1a and b might be explained by the different coordination of the Si atoms which are involved. In Fig. 1a this are Si atoms which already have three bonds formed within the clusters, while in Fig. 2b the “reacting” Si atoms have a lower coordination. Accordingly, for the latter case a bond is formed. We consider these two reaction channels as the most favorable ones. Other channels were attempted but during the approach clusters had the tendency to rearrange to a configuration similar to the one in Fig. 1b.

Important in Fig. 1b 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 reaction channels the calculation predict a repulsive interaction at low temperatures.

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 of these clusters

with the substrate is weak and no change of the geometric and electronic structure of the Si_4 is to be expected. In addition, most likely the clusters lie flat on the surface, are highly mobile at room temperature and approach each other in geometries similar to the ones calculated above. The samples are studied using XPS and only the peak corresponding to the 2p core level of Si is examined in detail (Fig. 2). The area of this feature corresponds to the amount of Si deposited on the HOPG. For clean bulk Si an almost symmetric peak centered at a binding energy of 99.4 eV is observed (Fig. 2c). For the deposition of Si atom ions on HOPG (Fig. 2b) a similar peak is observed with a shoulder corresponding to an unresolved feature at 101eV binding energy. For Si_4 clusters deposited on HOPG (Fig. 2a) a shift of the main peak of 0.5 eV towards higher binding energy and a slightly more intense shoulder corresponding to a broad peak around 102 eV is observed.

The small features at binding energies around 101-102eV are assigned to Si atoms bound to carbon atoms. The chemical shift depends on the coordination number (e.g., $\text{Si}_2\text{-C}$, Si-C or Si-C_2). Some atoms and clusters migrate to monoatomic steps and defects on the HOPG surface and form a covalent bond with carbon atoms there. The main peak corresponds to Si atoms bound to Si atoms. The observed shift of 0.5eV 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 large bulk like islands [11]. In our case the clusters are mobile on the surface [9,11] but the shift does not vanish with time. In case of the deposited atoms there is no such shift with respect to the bulk reference sample corresponding to the formation of large 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 a different sample: amorphous carbon. This surface consists of very small graphitic sheets with no ordering and the number of dangling carbon bonds is extremely high. This surface is more reactive than HOPG and might bind adsorbates easily. We generated this surface by sputtering HOPG with Ar ions at a kinetic energy of 1keV. For this surface, we find a sticking coefficient of 50% for the Si_4 cluster ions in fair agreement with earlier studies [13]. Fig. 3 displays the corresponding XPS data in comparison with the Si 2p bulk feature. As expected, for the deposition of Si atom ions (Fig. 3b) at low coverages of up to 4% ML 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. 3a) does not exhibit a difference to the case of the HOPG surface (Fig. 2a). The tetramers do not react with defect sites of the amorphous carbon and do not coalesce as to be expected for “magic” clusters. Again, these finding supports our hypothesis, that Si_4 clusters are suitable as building blocks for a cluster material.

Finally, we discuss which criteria make a cluster to be a building block for a new material. In general, clusters are considered to be highly reactive because of the dangling bonds of the surface atoms. However, there are clusters, which have a closed electronic shell and a large gap between the highest occupied and the lowest unoccupied molecular orbitals (HOMO-LUMO gap). It is well known, that these clusters have a low reactivity towards, e.g., O_2 .

There is a certain “activation” energy necessary to break off the closed shell corresponding to a barrier against any reaction. For example, the HOMO-LUMO gap for gas phase Si_4 [4,5] is of the same order as for C_{60} [3]. If our experimental and theoretical hints towards the existence of such a barrier turns out to be correct and a Si_4 cluster material could be synthesized, many other magic clusters with large gaps known from gas phase experiments like C_{32} and Al_{13}H may form such materials.

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 clusters material consisting of pure silicon. In the calculations a repulsive barrier has been found in the interaction potential, which 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. In contrast, Si atoms readily coalesce to such islands at the same conditions. The experimental and the theoretical data on its own we do not consider to be a prove of our hypothesis. However, there is a considerable agreement between these first theoretical and experimental results which we think is encouraging. If it will finally turn out to be really possible to synthesize such a material this will open a door to a whole new world of material science based on the many magic clusters already found in the gas phase.

We gratefully acknowledge useful discussions with W. Andreoni and A. Curioni. Support by the SFB 513 and computer time from the SSC Karlsruhe is gratefully acknowledged.

-
- [1] H.W. Kroto et al., *Science* **242**, 1139 (1988).
 - [2] M.S. Dresselhaus, G. Dresselhaus, and P.C. Eklund, “Science of Fullerenes and Carbon Nanotubes”, Academic Press, San Diego, 1995.
 - [3] H. Kietzmann, R. Rochow, G. Ganteför, W. Eberhardt, K. Vietze, G. Seifert, P.W. Fowler, *Phys. Rev. Lett.* **81**, 5378 (1998).
 - [4] O. Cheshnovsky, S.H. Yang, C.L. Pettiette, M.J. Craycraft, Y. Liu, and R.E. Smalley, *Chem. Phys. Lett.* **138**, 119 (1987).
 - [5] J. Müller, Bei Liu, A.A. Shvartsburg, S. Ogut, J.R. Chelikowsky, K.W.M. Siu, Kai-Ming Ho, and G. Ganteför, *Phys. Rev. Lett.* **85**, 1666 (2000).
 - [6] S.N. Khanna and P. Jena, *Chem. Phys. Lett.* **218**, 383 (1993).
 - [7] S. Burkart, N. Blessing, B. Klipp, J. Müller, G. Ganteför, and G. Seifert, *Chem. Phys. Lett.* **301**, 546 (1999).
 - [8] U. Röthlisberger, W. Andreoni, and M. Parrinello, *Phys. Rev. Lett.* **72**, 665 (1994).
 - [9] B. Klipp, M. Grass, J. Müller, D. Stolcic, U. Lutz, G. Ganteför, T. Schlenker, J. Boneberg, and P. Leiderer, *Appl. Phys. A* **73**, 547 (2001).
 - [10] P. Scheier, B. Maersen, M. Lonfat, W.-D. Schneider, and K. Sattler, *Surf. Sci.* **458**, 113 (2000).
 - [11] W. Yamaguchi, K. Yoshimura, Y. Maruyama, K. Igaraschi, S. Tanemura, and J. Murakami, *Chem. Phys. Lett.* **311**, 415 (1999).
 - [12] S.J. Carroll, S.G. Hall, R.E. Palmer, and R. Smith, *Phys. Rev. Lett.* **81**, 3715 (1998).
 - [13] J.E. Bower and M. Jarrold, *J. Chem. Phys.* **97**, 8312 (1992).
 - [14] J.P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

- [15] H. Grönbeck and W. Andreoni, Chem. Phys. **262**, 1 (2000).
- [16] H. Grönbeck, A. Curioni, and W. Andreoni, J. Am. Chem. Soc. **122**, 3839 (2000); W. Andreoni, A. Curioni, and H. Grönbeck, Int. J. Quant. Chem. **80**, 598 (2000).
- [17] D. Fischer, W. Andreoni, A. Curioni, H. Grönbeck, S. Burkart, and G. Ganteför, preprint.
- [18] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
- [19] Calculations used the CPMD code by J. Hutter: CPMD 3.0 Copyright IBM Corporation (1990-1997) and MPI Festkörperforschung Stuttgart, 1997.
- [20] Si PBE pseudopotentials and cluster structures from W. Andreoni (to be published).
- [21] W. Yamaguchi, K. Yoshimura, Y. Tai, Y. Maruyama, K. Igarashi, S. Tanemura, and J. Murakami, J. Chem. Phys. **112**, 9961 (2000).
- [22] W. Eberhardt, P. Fayet, D.M. Cox, Z. Fu, A. Kaldor, R. Sherwood, and D. Sondericker, Phys. Rev. Lett. **64**, 780 (1990).
- [23] G.K. Wertheim and S.B. DiCenzo, Phys. Rev. B **37**, 844 (1988).
- [24] W. Andreoni and G. Pastore, Phys. Rev. B **41**, 10243 (1990).

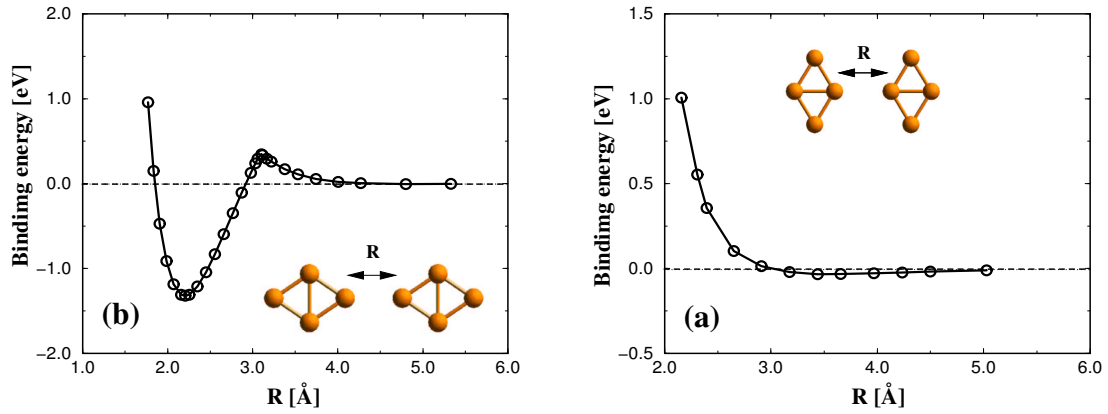


FIG. 1. Calculated potential energy curves for two neutral intercalating Si₄ clusters. Two different reaction channels have been calculated: the two tetramers approaching each other with the flat (a) and sharp (b) corners ahead. Case (a) is repulsive, while in case (b) a bond is formed. In (b) an energy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

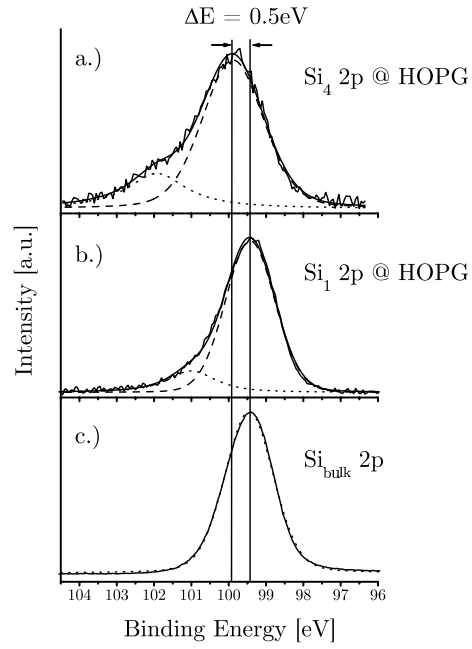


FIG. 2. XPS spectra of the Si 2p peak recorded for (a) Si_4 clusters deposited at 5eV onto HOPG (2% coverage), (b) positively charged Si atoms deposited at 5eV onto HOPG (2% coverage) and (c) for a Si bulk reference sample. Fits of the experimental data are also displayed in the figure.

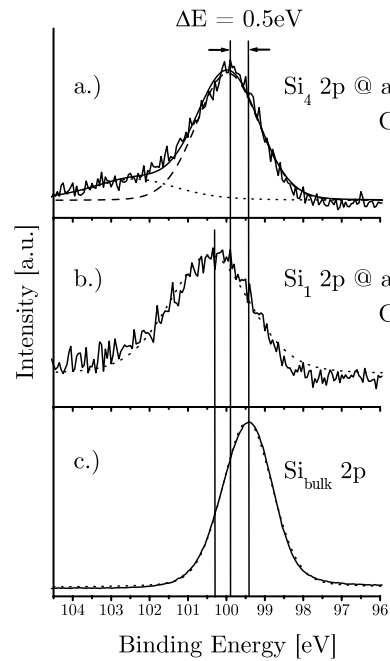


FIG. 3. XPS spectra of the Si 2p feature recorded for (a) Si_4 clusters deposited at 5eV onto amorphous carbon (4% coverage), (b) positively charged Si atoms deposited at 5eV onto amorphous carbon (3% coverage) and (c) for a Si bulk reference sample.