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Experimental and theoretical studies of interactions between Si_7 clusters

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Abstract. The possibility of using magic Si_7 clusters to form a cluster material was studied experimentally and theoretically. In experiments Si_7 clusters were deposited on carbon surfaces, and the electronic structure and chemical properties of the deposited clusters were measured using X-ray photoelectron spectroscopy (XPS). A non bulk-like electronic structure of Si_7 was found in the Si $2p$ core level spectra. Si_7 is suggested to form a more stable structure than the non-magic Si_8 cluster and Si atoms upon deposition on carbon surfaces. Theoretically it was possible to study the interaction between the clusters without the effect of a surface. Density functional theory (DFT) calculations of potential curves of two free Si_7 clusters approaching each other in various orientations hint at the formation of cluster materials rather than the fusion of clusters forming bulk-like structures.

PACS. 31.15.Ew Density-functional theory – 33.60.Fy X-ray photoelectron spectra – 34.20.Cf Interatomic potentials and forces – 36.40.-c Atomic and molecular clusters

1 Introduction

In the cluster size regime below ∼100 atoms, every additional atom can change the chemical and physical properties of the clusters completely. Among various clusters, so-called magic clusters are of particular interest due to their high stability and inertness. Magic clusters are often suggested to be promising candidates as building blocks of cluster materials. The high stability and inertness of magic clusters are due to electronic or geometric effects:

- closed electronic shells analogous to the electronic configurations of inert gas atoms, generally indicated by a large gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO gap);
- closed geometric structures such as clusters with 13 or 55 atoms with icosahedral shape.

When two magic clusters approach, either they can merge forming a bulk-like structure, or remain separated due to significantly high activation barriers for the fusion of the clusters. In the latter case, one may expect formation of a cluster material, i.e. a new material showing characteristics dissimilar to those of the known bulk materials consisting of atoms of the same element.

Efforts have been made in the past to find magic clusters forming cluster materials. Besides fullerene, which can form a fullerite structure, a C_{60} crystal, it was previously shown that Sb_4 can be periodically ordered on some surfaces, forming a two dimensional cluster material [1,2]. Using Photoelectron Spectroscopy in combination with Density Functional Theory (DFT) calculations, Si_4 was suggested to be able to form cluster materials [3].

In the present work, Si_7, another magic cluster with a large HOMO-LUMO gap of 1.5 eV, which is even higher than the bulk band-gap of 1.1 eV was deposited on carbon surfaces, and the electronic structure as well as the inertness of the clusters were studied using X-ray photoelectron spectroscopy (XPS) [4,5]. We show experimental hints of magic Si_7 clusters being more inert on the surface than the non-magic Si_8 clusters. While in experimental approaches the clusters have to be deposited on a surface, theoretical studies focus on the behavior of two pure Si_7 clusters without the effects of a surface. The theoretical approach addresses directly the question of the usefulness of magic Si_7 clusters as building blocks for cluster materials, which is the main objective of the present study. DFT calculations on free Si_7 clusters were performed, indicating that Si_7 clusters can survive as individual clusters without fusing. Even though a full computation of the effect of the surface on the properties of Si clusters is very time consuming and was not intended here, preliminary theoretical studies [12] indicate that the effect of the weakly interacting HOPG surface used in the experiments on the structural and electronic properties is very small.

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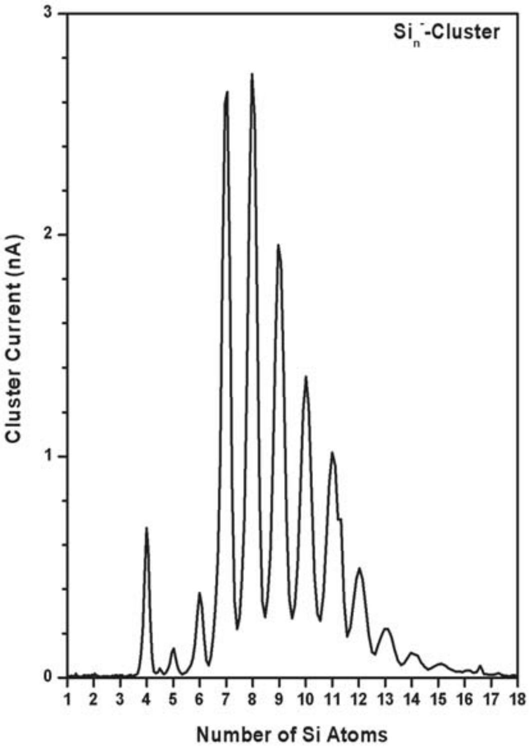

Fig. 1. Mass spectrum of Si cluster anions in the gas phase obtained in the experimental set-up used in the present work.

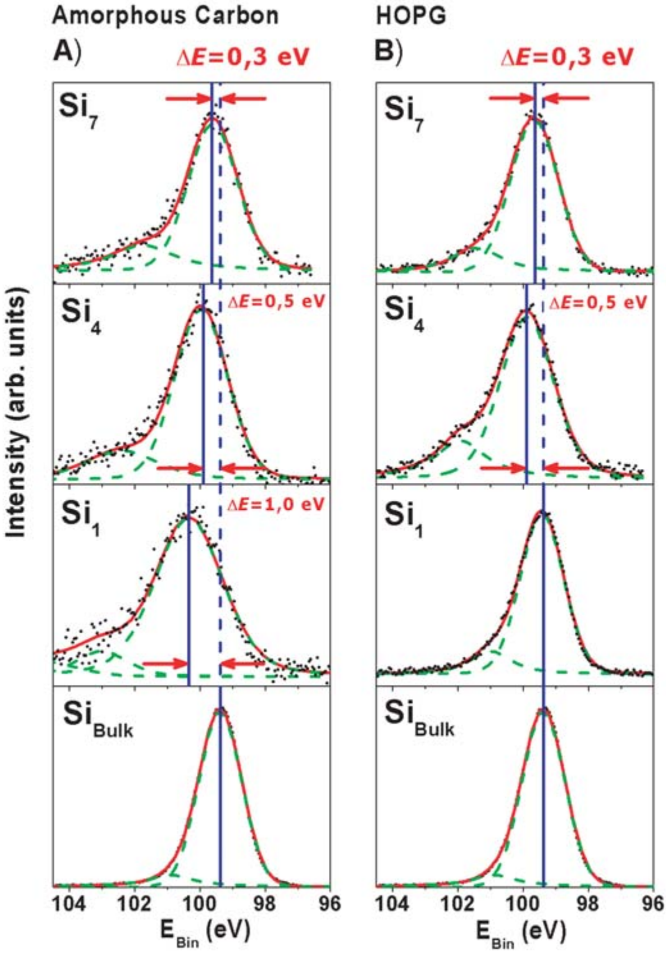

Fig. 2. (Color online) XPS Si 2*p* core level spectra of Si, Si_4 and Si_7 clusters deposited on (A) amorphous carbon; (B) HOPG.

2 Technical details

2.1 Experiments

The experimental set-up has been described in detail elsewhere [6]. Briefly, cluster ions are generated using a magnetron-sputter source and are then mass-separated by a 30° sector magnet [7]. The anions are decelerated to a kinetic energy of less than 0.3 eV per atom and soft-landed on highly oriented pyrolytic graphite (HOPG) and amorphous carbon surfaces (heavily sputtered HOPG). As shown in Figure 1, our instrumental resolution is high enough to deposit fully mass-selected Si clusters consisting of less than ~10 atoms. Si clusters are found to be very clean in the gas phase. The clusters on the surfaces are analyzed in an ultrahigh-vacuum chamber (UHV) system with a base pressure of 3×10^{-10} mbar. It is equipped with an X-ray source with an aluminum/magnesium anodes and a cylindrical hemispherical analyzer for XPS measurements. An ion gun is also installed in the chamber, which is used to create amorphous carbon surfaces by sputtering clean HOPG surfaces. All measurements are carried out at room temperature.

2.2 Theory

For the calculations, the Car-Parrinello molecular dynamics (CPMD) package, an implementation of DFT was used [8]. Calculations were performed using norm conserving pseudo potentials of Troullier-Martins type and a generalized gradient corrected exchange correlation functional as suggested by Perdew, Burke, and Ernzerhof (PBE) [9,10]. The plane wave basis set used had a kinetic energy cutoff of 20 Ry. Tests with a higher cutoff did not change the results significantly. Periodic boundary conditions were employed and the simulation box was a cuboid of $40 \times 20 \times 20$ Å^3.

3 Results and discussions

3.1 Experimental studies

Previously, Si_4 clusters on carbon surfaces were studied and the possibility for using Si_4 clusters as building blocks for a cluster material has been indicated [3]. In the present work, similar experiments to those in reference [3] were performed with Si_7, which is another magic Si cluster as free species: Si_7 clusters were deposited on carbon surfaces and the results were compared to those of deposited Si atoms (Fig. 2). When Si_7 is deposited on HOPG, the Si 2*p* peak in the XPS spectra is slightly shifted to a higher binding energy compared to the Si bulk value as well as

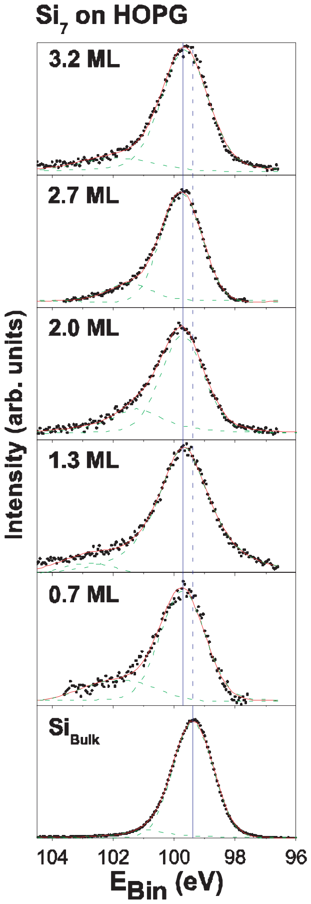

Fig. 3. (Color online) XPS Si 2p core level spectra of Si$_7$ clusters deposited on HOPG for various Si coverages.

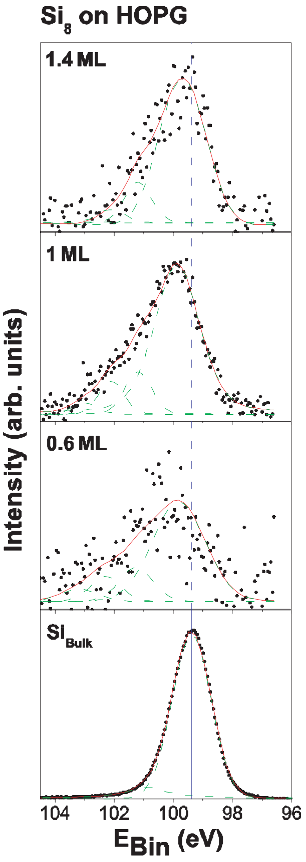

Fig. 4. (Color online) XPS Si 2p core level spectra of Si$_8$ deposited on HOPG for various coverages. The emerging of additional shoulders in the curves indicates reactions with the residual gas.

deposited Si atoms. When Si$_7$ clusters are deposited on amorphous carbon surfaces, the binding energy of the Si 2p state is almost the same as that of Si$_7$ deposited on HOPG. In contrast, deposition of Si atoms on amorphous carbon yields SiC formation, which can be identified by a positive Si 2p core level shift of 1 eV with respect to the Si bulk value. Deposition of Si$_7$ clusters seems to form a structure substantially resistant towards carbide formation. One can suggest that Si$_7$ either survives as an individual cluster upon deposition, or Si$_7$ can be fragmented to two of more stable Si clusters, for example the fragmented species on carbon such as Si$_2$ and Si$_5$, or Si$_3$ and Si$_4$ can be stable and resistant towards carbide formation.

Regarding the origin of the positive core level shift observed for the deposited Si$_7$ clusters with respect to the bulk value, one may argue that the deposition of magic clusters results in fusion of clusters, forming islands with a bulk-like structure, which could lead to a similar core level shift. Previously, core level shifts for metal islands smaller than ~10 nm in size have been found, which can be explained by taking many different effects into account, such as lattice strain, metal-insulator transition, metal-support interaction, and final state screening [11]. It is, however, important to note that there is no core level shift depending on Si coverage (Fig. 3). Since different Si coverage would result in various particles sizes, variation of Si coverage should lead to core level shift, which cannot be observed experimentally. Therefore, small sizes of bulk-like Si nanoparticles cannot be the origin of the positive core level shift we observe in Figure 2. Rather, it seems that all Si$_7$ clusters should form a non-bulk-like structure.

For comparison, non-magic Si$_8$ clusters were deposited on HOPG (Fig. 4). XPS spectra show a similar Si 2p core level shift to that of Si$_7$, but they show additional shoulders at higher binding energies. There are several possibilities for rationalizing those shoulders in the Si 2p spectra. The appearance of the shoulder may point to a significant contamination of the clusters by the residual gas in the chamber such as water. During the deposition of clusters, the partial pressure of the UHV chamber ($\sim 1\times 10^{-9}$ mbar) is higher than the base pressure, and therefore unstable clusters may be easily contaminated by the residual gas. Within this scenario, one may argue that the structure formed by deposition of Si$_7$ is more stable that that of Si$_8$. One may also argue that there is a fragmentation process of Si$_8$ on the surface, and the fragmentation is not uniform but random so that Si clusters with many differently sized clusters form, resulting in the appearance of the heterogeneity in the core level spectra. The shoulders are more pronounced for Si$_8$ than Si$_7$, and it might be that Si$_7$ either does not fragment or fragments more uniformly to specific cluster sizes.

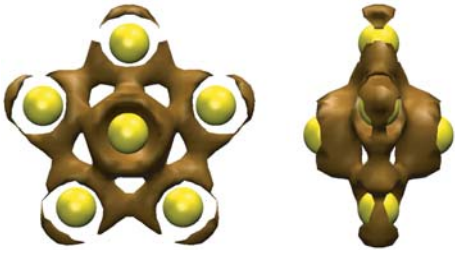

Fig. 5. (Color online) Ground state geometry and electron density ($\rho = 0.0059$) of a Si_7 cluster.

3.2 Theoretical studies

The main objective of the present study is the question on the usefulness of magic Si_7 clusters as building blocks for cluster materials. In order to address this question, the theoretical studies focus on the behavior of two pure Si_7 clusters without the possibly disturbing effect of surfaces. Since experimental approaches to the main objective cannot avoid the effect of surfaces, at least only weakly interacting surfaces have to be considered in the experiment. The limiting behavior of the system without surfaces is thus approximated by the experimental studies as closely as possible. A full computation of the effect of a surface on the properties of Si clusters, on the other side, is very time consuming and was not intended in the present work. Preliminary theoretical studies [12] by the methods used here, however, indicate that the effect of an HOPG surface on the structural and electronic properties is very small.

Previously two Si_4 clusters approaching each other in various orientations were studied theoretically in order to shed light on activation barriers, which may hinder fusion of magic clusters [3]. The primary goal of our present work is to extend our theoretical studies to other magic Si clusters such as Si_7. Since experiments as well as preliminary theoretical studies [12] of isolated Si_4 clusters on HOPG indicate that the cluster-graphite interaction is very weak we investigate the interaction of two clusters without any substrate.

Figure 5 shows the ground state structure of a Si_7 cluster together with its electron density. This structure was computed using CPMD's default algorithm [8] to optimize the geometry and is consistent with other published results [13–15].The cluster forms a pentagonal bipyramid with characteristic inter-atomic distances between 2.4 and 2.5 Å. For two clusters with this structure there are several reaction channels, i.e. the clusters can approach each other in various orientations.

One of them is shown in Figure 6, where one of the atoms in the pentagonal plane of one cluster approaches the atom at the top of the other cluster ("head-top" configuration). The only restriction in this simulation was to fix the two nearest atoms to get a well defined reaction coordinate R, which is the distance between these atoms. The "potential" energy shown in the diagrams is the result of geometry optimizations for various distances R and calculated as

$$E_p = E(\text{system}) - 2E(\text{single cluster}). \qquad (1)$$

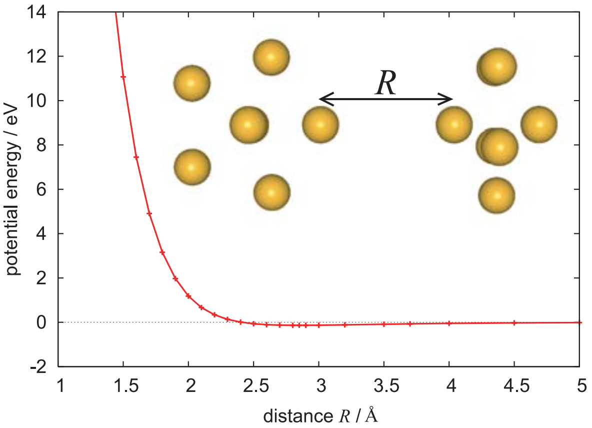

Fig. 6. (Color online) Potential energy of two Si_7 clusters approaching each other in a "head-top" configuration. In this case the two nearest atoms of the clusters are kept fixed to get a well defined reaction coordinate R. Including the Local Spin Density Approximation, as provided by CPMD, did not result in visible changes in the potential energy. For more details, please see text.

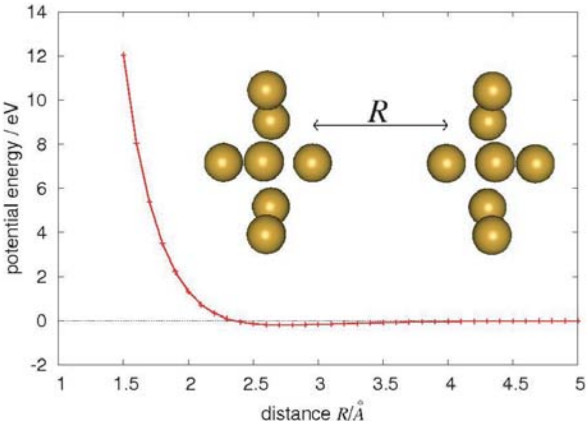

Fig. 7. (Color online) The potential curve of two Si_7 clusters approaching in a "top-top" configuration. As in Figure 6 the two nearest atoms between the clusters are kept fixed.

This reaction channel is important to look at, since occupied states of the first cluster overlap with the LUMO of the second. Even in this case though, there is a mainly repulsive interaction between the clusters. A shallow minimum is observed at a distance of $R = 2.9$ Å.

In Figure 7, the clusters were oriented differently such that the atoms on top of the pyramids approached each other. In this case a shallow minimum of the energy curve can be found at 2.7 Å, which can be considered to be the equilibrium distance between two clusters with this orientation. Looking at the electron density in Figure 5 one can see that there is much less density at the bipyramid's tops than at the pentagon's angles. The strong repulsion can be seen as a result of the Coulomb interaction between the two nuclei.

Calculating three other reaction channels not shown here, similar behaviors with less pronounced or no potential minima were found. One of them, where both clusters were assumed to approach with one atom in the pentagonal plane of each cluster directed to the other cluster ("head-head" configuration), features a metastable state, having an energy of 0.6 eV at a cluster-cluster distance of 2.2 Å. In this state the structure of each cluster is more compact than the ground state structure. Due to a reaction barrier of about 0.75 eV it cannot be reached by cluster diffusion at room temperature. The potential energy of this reaction channel does not become negative.

4 Conclusion

Using XPS, different electronic structures for deposited Si_7 clusters and Si bulk were observed. Moreover, deposited Si_7 clusters were found to be more inert than the non-magic Si_8 clusters and Si atoms. The formation of Si_7 cluster materials is supported by DFT calculations in which no reaction channel leading to the fusion of two clusters could be found.

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