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Theoretical study of small silicon clusters on a graphite layer

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Abstract. In a series of recent experiments, the HOMO-LUMO energy gaps of small Si clusters deposited on a graphite substrate have been determined by Scanning Tunneling Microscopy (STM). The values obtained were found to be substantially smaller than the energy gaps of corresponding passivated clusters. This work considers dimensional reduction as a possible mechanism for a sizeable energy gap narrowing by the example of the system Si_5. The impact of the graphite substrate on the deposited species is investigated in the framework of a pseudocluster model.

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

A large number of contemporary research efforts, both experimental and theoretical, are concerned with the basic properties of Si clusters and nanostructures which are of high relevance to present applications in microelectronics as well as to future developments of this technology. In a recent STM study [1], small Si clusters (Si_N) have been investigated on a Highly Oriented Pyrolytic Graphite (HOPG) substrate. In these measurements, the capability of STM technique for determination of the energy gap size of deposited clusters has been used. The Si_N clusters were generated through an atomic deposition procedure involving magnetron sputtering of pure Si [2]. As the atomic Si vapor is deposited on the HOPG surface, Si atoms can conglomerate through a diffusion process followed by quasi-free growth. The microscopically detected Si_N clusters were classified according to their approximate diameters ranging from 2.5 to 40 Å. In all cases considered, the energy gaps determined were found to be sizably smaller than that of bulk silicon (1.1 eV). A critical cluster size of 15 Å was identified beyond which a vanishing energy gap was detected. For smaller cluster diameters, the largest recorded gap amounts to 450 meV.

These results imply a reversal of the commonly assumed trend of an energy gap increase as one goes from the infinite system to its finite counterparts, as far as deposited clusters are concerned. For Si_N clusters in the gas phase, a high degree of reconstruction has been confirmed [3], associated with the flexibility of cluster systems that allows for elimination of dangling bonds through geometric rearrangement. Thus, for Si_N clusters with $N < 20$, comparatively large HOMO-LUMO energy differences in the order of 3 to 4 eV have been found. For the larger ones among the Si_N clusters investigated in the indicated STM experiment, the geometry of Si bulk fragments has been proposed which have been shown computationally [4] to exhibit vanishing HOMO-LUMO differences if they are not passivated through addition of hydrogen atoms. Still, the question why the deposition of Si atoms on HOPG should give rise to the formation of unreconstructed Si bulk fragments remains to be answered by computational theory.

The present work follows a different purpose. We will concentrate on the regime of Si_N clusters distinctly smaller than the critical size of 15 Å in diameter. More specifically, we will propose a model that in principle allows for the characterization of the interaction between the deposited cluster and the HOPG substrate, namely the Partial Density of States (PDOS) and the Partial Overlap Density of States (PODOS) analysis of Si_N units attached to a pseudocluster consisting of a hydrogen passivated graphite fragment [5,6]. In the framework of this approach, we will discuss dimensional reduction as a possible mechanism of energy gap decrease by the example of the Si_5 cluster. The choice of Si_5 is motivated by the fact that both three- and two-dimensional stable isomers have been isolated for this species [7]. Thus, this study is guided by a twofold intention: (a) introduction of a general computational model for the interaction between Si_N systems and graphite substrates, (b) application of this model to one specific case, namely Si_5, in an attempt to make contact with STM measurement.

For all species considered, full all-electron geometry optimizations were carried out. The quantum chemical procedure employed was Becke's three parameter hybrid

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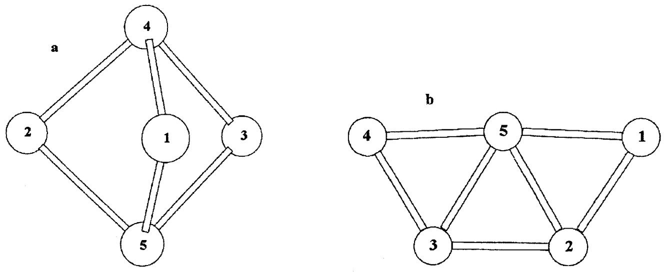

Fig. 1. (a) Equilibrium geometry of Si_5. (b) Equilibrium geometry of the most stable Si_5 isomer.

method in conjunction with the correlation functional of Lee, Yang and Parr [8]. For the pure Si_5 clusters, a 6-31G* basis set was used which has been demonstrated in the past to be an adequate choice for the treatment of Si clusters [9].

For the simulation of the substrate, we used a C_{54} planar graphite fragment terminated by 18 hydrogen atoms. This is an extension of a model that has been used in the past to investigate the reaction of various species with a graphite layer [5]. This representation of the substrate was subjected to a test in which the widths and the onset energies of the σ and π bands extracted from our model by means of PDOS analysis were compared with results of band structure calculations [10]. It was found that both approaches agree within an error margin of approximately 0.2 eV. Similarly, the transition to the sizably larger pseudocluster $C_{96}H_{24}$ introduced only minute shifts in the indicated energy band parameters.

In view of their considerable size, for all composite systems to be discussed in the following section, *i.e.*, $SiC_{54}H_{18}$ and $Si_5C_{54}H_{18}$, a 3-21G* basis has been used which has been shown elsewhere [11] to yield very satisfactory approximations to the 6-31G* results for small Si clusters. In all computations reported here, the program Gaussian 98 [12] was utilized.

We will first present our results on pure Si_5 clusters and in a subsequent step comment on the interaction between a Si_5 unit and a graphite substrate. A structure of D_{3h} symmetry has been identified as the most stable geometry for this system [9,13]. According to the comprehensive Density Functional Theory based study of Fournier *et al.* [7], the geometry of second highest stability is planar, emerging from edge-capping of the highly stable Si_4 rhombus with one Si atom. For a comparison of both structures, see Figs. 1a, 1b. Our calculation yields for the three-dimensional ground state geometry a binding energy of 2.85 eV/atom which deviates by about 2% from the value reported by Raghavachari [9], 2.78 eV/atom, as obtained by use of the MP4/6-31G* method.

For further comparison of the two geometric variants of Si_5, it is instructive to study the PDOS spectra of these species in the energy region around the HOMO-LUMO gap, as displayed in Figs. 2a, 2b. Focusing first on the spectral features of the D_{3h} alternative (Fig. 2a), one notices a large HOMO-LUMO gap size, amounting to 3.2 eV. While the dominating peaks of the valence electron region are of s and p_{xy} symmetry, a pronounced p_z contribution can be discerned at about 2.5 eV below the Fermi energy which in this representation is equated to zero. This p_z peak is attributed to a D_{3h} doublet of the three equatorial atoms which form an equilateral triangle (see Fig. 2a). In case of the planar structure, we also find two valence orbitals predominantly composed of p_z electrons. However, in contrast to the three-dimensional variant, these two orbitals, indicated by two narrow peaks in Fig. 2b, are not degenerate but exhibit an energy separation of 2.3 eV. While the lower one of these orbitals consists of a totally symmetric π bond, the one corresponding to higher energy describes bonding interaction between the atoms Si_1 and Si_2 as well as between Si_3 and Si_4 (see Fig. 1b), but the interaction between these two atom pairs is repulsive. The PDOS peak associated with the latter orbital is located in the energy gap region of the D_{3h} variant. The resulting effect

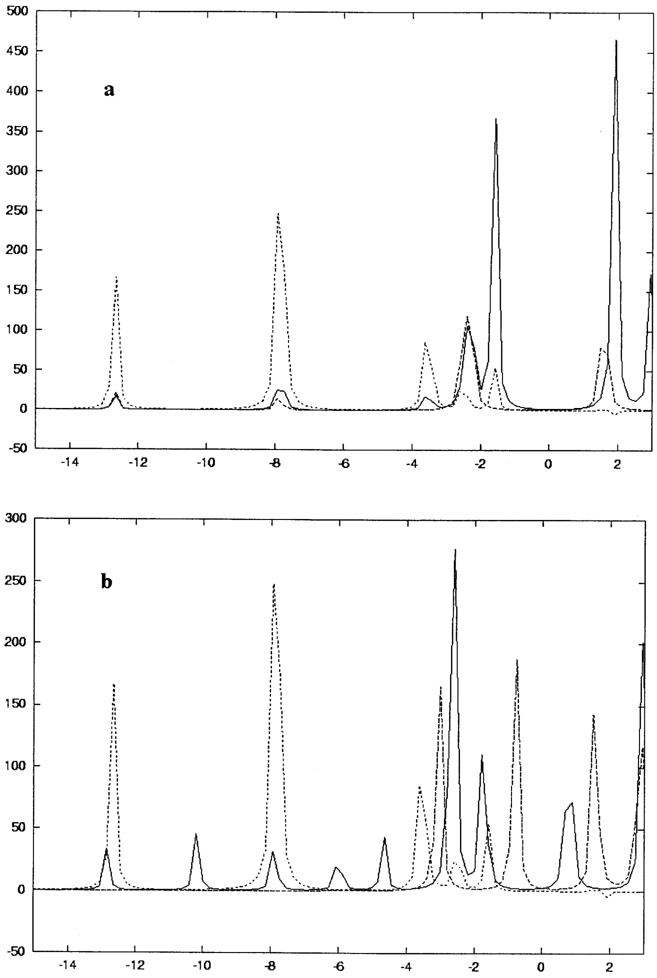

Fig. 2. (a) Valence electron DOS spectrum for the ground state of Si_5. Shown are the contributions of p_{xy} orbitals (solid line), p_z (dashed line) and s (dotted line) orbitals. (b) Valence electron DOS spectrum for the most stable planar isomer of Si_5. The assignments of the three lines shown are as in (a).

Table 1. Parameters for $SiC_{54}H_{18}$.

Site of Si	Spin	E^a_{ads} [eV]	D^b [Å]
Hole	0	0.08	3.20
Edge	0	0.93	2.00
Particle	0	0.97	2.37
Hole	1	0.07	3.20
Edge	1	0.14	2.34
Particle	1	0.19	2.71

[a] Adsorption energy of Si on $C_{54}H_{18}$.

[b] Vertical distance of Si from the plane of $C_{54}H_{18}$.

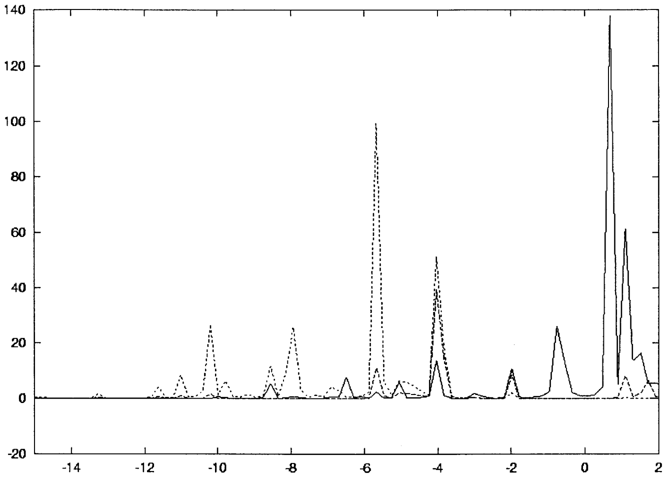

Fig. 3. Valence electron DOS spectrum for the particle site of $SiC_{54}H_{18}$ in singlet spin configuration. Shown are the contributions of p_{xy} orbitals (solid line), p_z (dashed line) and s (dotted line) orbitals.

of HOMO-LUMO gap narrowing is enhanced by a PDOS maximum with p_{xy} symmetry which is found at a lower energy as compared to the three-dimensional case, thus setting an upper limit for the gap from above. The gap size found for the planar isomer is 1.61 eV. In summary, the HOMO-LUMO energy difference is seen to decrease by 50% as one goes from the three-dimensional ground state of Si_5 to the planar isomer of lowest energy.

On the background of these observations made on pure Si_5 clusters, we want to turn now to the situation of an Si_5 unit deposited on a $C_{54}H_{18}$ pseudocluster which is more suitable to simulate the experimental condition than the isolated species. However, for a better understanding of the possible impact of the substrate on the adsorbed cluster, we investigated first the interaction of a single Si atom with the $C_{54}H_{18}$ system. As a Si atom prefers triplet ($S = 1$) over singlet ($S = 0$) spin configuration, both alternatives have to be taken into consideration. Consequently, full geometry optimizations were performed for the system $SiC_{54}H_{18}$ in $S = 0$ and $S = 1$ conditions. Selecting the initial geometries for these computations, we chose three different plausible test sites of an Si atom on the graphite network: (a) a hole site, Si being placed above the center of a C_6 hexagon, (b) an edge site, Si located above the midpoint of a C-C bond, and (c) a particle site, where the position of Si is vertically above a C atom. The six emerging cases are listed in Table 1. For both the spin singlet and triplet configurations, the hole site results with highest total energy, corresponding to a maximum distance of the adsorbed Si atom from the $C_{54}H_{18}$ substrate, as documented in Table 1. We also indicate the adsorption energies for the different cases considered. Under the aspect of this quantity, the particle site appears to be slightly preferred over the edge site. From the values indicated in Table 1, the singlet is obviously more favorable than the triplet spin condition throughout.

For qualitative evaluation of the impact of the graphite layer on the adsorbed Si atom, we present in Fig. 3 the PDOS of the Si valence electrons for the particle site in spin singlet condition which has emerged with highest adsorption energy from our investigations. As is inferred from the figure, the sharp s, p_{xy} and p_z lines of an isolated Si atom are spread out under the influence of the $C_{54}H_{18}$ substrate into broad distributions of s, p_{xy} and p_z character. Below an energy of about −6 eV, the spectrum is dominated by the s component with small admixtures of either p_{xy} or p_z symmetry. In the interval between −6 eV and the Fermi energy, the prevailing maxima contain all three components, s, p_{xy} and p_z, corresponding to electronic configurations of the sp^3 type. The highest PDOS peak in the bound region, however, is of pure p_{xy} character. The analysis of the respective molecular orbital reveals that it contains minimal admixtures of substrate states and thus does not contribute to the interaction between the adsorbate and the $C_{54}H_{18}$ layer. The energy gap which amounts to 1.3 eV is embedded into a p_{xy} continuum.

From our simulations, an Si atom attaches itself preferentially to a particle or an edge site of the graphite substrate. As these two situations do not differ strongly in the vertical height of the Si adsorbate from the $C_{54}H_{18}$ layer, it is plausible that the quasi diffusion process by which the experimentally detected clusters are generated could result in the formation of a planar unit. This assumption is supported by the experimental fact that a nearly planar Si_7 unit has recently been observed in an STM measurement with high spatial resolution [14].

In the following step, we considered a planar Si_5 cluster adsorbed to $C_{54}H_{18}$. We defined the initial geometry by selecting a set of five particle sites that optimally approximate the equilibrium structure of planar Si_5. Figs. 4a, 4b display the result of the full geometry optimization of the combined system. As demonstrated in Fig. 4a, the geometry of the isolated planar Si_5 unit is not strongly affected by the optimization. However, the geometric relaxation of the whole system leads from parallel orientation of Si_5 and $C_{54}H_{18}$ to a marked tilt of the Si_5 plane with respect to the substrate. The two Si atoms closest to the $C_{54}H_{18}$ layer are located in clearly identifiable particle sites. The

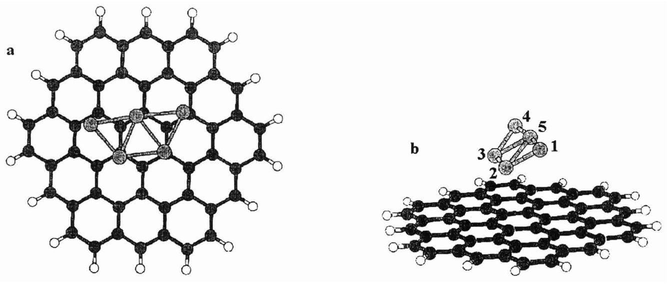

Fig. 4. Equilibrium geometry of $Si_5C_{54}H_{18}$. (a) Top view, (b) side view.

structural distortion of the substrate due to the presence of the adsorbate is small.

Fig. 5a contains the PDOS spectrum for the valence electrons of Si_5 adsorbed to $C_{54}H_{18}$. The profiles of the s, p_{xy} and p_z electron distributions resemble clearly those of the planar Si_5 isomer in the gas phase, as shown in Fig. 2a. In particular, the sizeable reduction of the HOMO-LUMO gap, which was found to be associated with the transition from the three-dimensional ground state to the planar isomer of Si_5, is preserved as the planar Si_5 cluster is deposited on the $C_{54}H_{18}$ substrate. In contrast to our findings related to the free Si_5 systems, however, for the composite case the maxima limiting the energy gap are not any longer purely of p_z and p_{xy} nature, but each of maxima contains both symmetries. The energy gap size is determined as 1.66 eV.

For a characterization of the interaction between adsorbate and substrate, the overlap density spectrum of $Si_5C_{54}H_{18}$ was examined, as shown in Fig. 5b. Specifically, the three curves displayed in the figure refer to the overlap between the s, p_{xy} and p_z Si valence electrons and the p_z electrons of $C_{54}H_{18}$. Obviously, in the region of the energy gap, all contributions are negative, which is a fingerprint of antibonding interaction. In the deeper lying energy regime between -10 and -4 eV, broad bands of bonding p_{xy} and p_z electrons of Si can be identified along with a predominantly antibonding s band. The fragile balance of bonding and antibonding components results in a small adsorption energy of 0.11 eV for the planar Si_5 isomer deposited on the $C_{54}H_{18}$ pseudocluster.

In conclusion, a pronounced decrease of the HOMO-LUMO energy gap has been found for pure Si_5 clusters as one goes from the three-dimensional ground state of the unit to its lowest lying planar isomer. From our investigation of an Si_5 species attached to a graphite substrate in the framework of a $Si_5C_{54}H_{18}$ pseudocluster model, we conclude that Si_5 may stabilize on a graphite surface in planar geometry, exhibiting a strongly diminished energy gap, as observed for the case of the planar species in the gas phase.

Thus, dimensional reduction of the Si cluster geometry appears as an efficient mechanism for energy gap size narrowing. The mode of cluster generation as realized in the STM experiment, *i.e.* atomic Si deposition followed by quasi-free cluster growth on a graphite surface, may naturally give rise to a preferred emergence of planar or quasi-planar species. At the same time, it has to be pointed out that the absolute value of the energy gap size of $Si_5C_{54}H_{18}$, as resulting from our study, still exceeds the experimentally secured data for this quantity by a considerable margin. However, the present computations do not aim at an exact quantitative agreement between measurement and theory, but rather focus on the elementary process of the experimentally established energy gap decrease in deposited Si clusters and on the suitability of the outlined pseudocluster approach for the description of small Si_N units adsorbed to graphite. As the gap size depends very sensitively on the precise orbital energies of states that appear in the HOMO-LUMO energy interval upon dimensional reduction, the numerical results of the

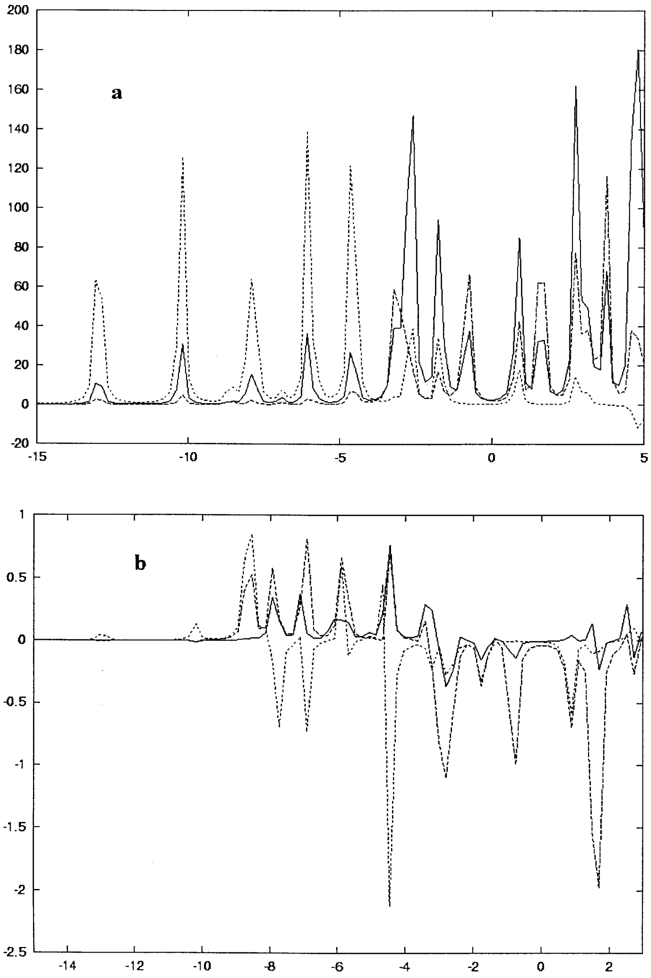

Fig. 5. (a) Valence electron DOS spectrum for $Si_5C_{54}H_{18}$ at equilibrium geometry. Shown are the contributions of p_{xy} orbitals (solid line), p_z (dashed line) and s (dotted line) orbitals of Si. (b) Valence electron PODOS spectrum for $Si_5C_{54}H_{18}$ at equilibrium geometry. The figure displays the overlap density of Si p_{xy} (solid line), Si p_z (dashed line) and Si s orbitals (dotted line) with the p_z orbitals of C.

present approach may be improved by use of a more accurate quantum chemical procedure. This could be achieved through the application of a higher electron correlation level and simultaneously a basis set of greater complexity than used in this work. In addition, theory should include the broadening of the experimental lines to make allowance for a realistic comparison with the measured data. These extensions of the work summarized here are presently under way.

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